FoU-projektet för papperskonservering

Ageing / Degradation of Paper

A literature survey

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CONTENTS

PREFACE

"FoU-projektet för papperskonservering" is a Swedish R&D-project on preservation and conservation. It is conducted by the National Archives, the Royal Library and the National Land Survey of Sweden together with some other major institutions responsible for the preservation of books and archival material.

This literature survey on the "Ageing/degradation of paper" has been prepared by the Swedish Pulp and Paper Research Institute (STFI) and the Swedish University of Agricultural Sciences (SLU) under the leadership of Professor Tom Lindström. It was originally published in Swedish in February 1988 as the first report within the project.

The report has attracted interest even outside the Nordic language sphere and it is clear that it meets a need which cannot to any great extent be satisfied merely by a short English summary. It has therefore been decided to publish an English translation of the report as a special Swedish contribution to the efforts of the international paper preservation community.

The translation has been carried out by Bristows Engelska Språktjänst.

Stockholm, September 1989

Ingmar Fröjd
Project Coordinator

SUMMARY

This literary survey summarizes the most important known facts concerning the ageing and degradation of paper.

The main chemical and physical mechanisms during ageing and degradation of paper can be considered to be qualitatively well known, but the complexity in the chemical and physical degradation processes is too great to permit a detailed understanding.

It is evident that acidic hydrolysis processes and oxidative attacks dominate. The hydrolytic and oxidative attacks are coupled since oxidation accelerates the hydrolysis and vice versa. Hydrolysis and oxidative attacks are followed by chemical crosslinking processes in the wood polymers and crystallization and hornification (physical volume relaxation) which are manifested in embrittlement and colour changes in the paper.

Microbiological attack takes place primarily in climates with a very high atmospheric humidity (tropical-subtropical) or in papers damaged by water.

The environment is of great importance for the ageing stability of paper. High temperature and high relative atmospheric humidity accelerate the breakdown processes. Variations in the relative humidity or in the temperature also accelerate the oxidation processes and the mechanical-chemical degradation of paper.

Environmental contamination (SO_2, NO_x) strongly accelerates the hydrolysis and oxidation reactions. Of great importance for the oxidation processes (including the oxidation of SO_2 to $SO_3(H_2SO_4)$) is the presence of trace metals, (transition metals) which autocatalyse the reactions.

The storage environment for paper can be improved by relatively simple means and such measures must in a larger perspective be weighed against e.g. mass deacidification of paper.

The selection of raw materials and environmental condi-

tions during the papermaking are of central importance for the ageing stability of paper.

The two most important factors for the production of durable papers are that the paper should contain an alkaline buffer ($CaCO_3$;$MgCO_3$) and should be manufactured from a raw material with as high a content as possible of unoxidized cellulose. The buffer capacity of the paper is more important than the pH-value of the paper, which in practice means that the paper should contain at least a few per cent $CaCO_3$ as filler in order to prevent acidification from environmental pollution and oxidized degradation products.

The emphasis on a pure fibre raw material means that paper manufactured from cotton cellulose is more durable than paper manufactured from conventional bleached kraft or sulphite pulp, which in its turn is better than so-called wood-containing paper.

Archive papers which are today manufactured from pure cotton raw material with an alkaline buffer (ca. 3% $CaCO_3$) constitute, because of their price, a very small and exclusive part of the so-called white paper sector. Large important contributions can therefore be made through better specification of paper for everyday use, since there are probably great differences in ageing stability between different grades. Here research and development work is required e.g. to elucidate the effect of modern bleaching sequences on the ageing stability of paper and so on.

A correlation seems to exist between accelerated ageing tests and natural ageing of paper. Such ageing tests should however be looked upon as a complement to quality profiles of paper and not as a decisive measuring method.

With the methods used today, a degraded paper cannot be restored, but its rate of degradation can be reduced. The only methods which exist today for reducing the breakdown of paper are the so-called deacidification methods where the aim is to neutralize acidic residues in the paper and to deposit an alkaline buffer in the paper.

Good liquid-based deacidification methods for single pages in books exist today while methods for so-called mass deacidification are still in a development stage. The methods being discussed or used today are on the one hand the so-called DEZ-method, where diethyl zinc is added to dry paper in the gas phase, and the so-called "Wei T'o way" where methylmagnesium carbonate dissolved in freon is used. In the case of the DEZ-method, there are several process technical problems (explosion risk, toxicity), and the reaction product from the process is not an established ageing inhibitor. The primary disadvantage of the "Wei T'o"-method seems to be in the use of freons, which for environmental reasons have a very uncertain future. Alternatives to freons are therefore interesting development routes for this process.

From a research and development viewpoint in the paper conservation field, the following general assessment can therefore be made:

It must be important to give high priority to diagnostic, non-destructive analytical methods for assessing the condition and ageing stability of paper. With a reasonable effort and modern analytical instruments it should be possible to improve the present arsenal considerably.

It is also important to obtain a better technical assessment of present deacidification methods, and to develop, improve and implement such techniques in practical use.

For the future it seems very important to develop ageing stable papers based not on exclusive raw materials such as cotton, but on e.g. wood-based raw materials. This work is to a certain degree a question of technical development but there is also an educational aspect which is well suited for qualified committee work.

Today it is difficult to imagine that basic research efforts with limited financial backing will revolutionize paper conservation work, but it is nevertheless important to develop greater competence in this area and to initiate basic research in this area at institutes and universities.

1 EFFECTS OF AGEING ON THE MECHANICAL AND OPTICAL PROPERTIES OF PAPER

1a Introduction and short historical survey

Paper made by hand during the middle ages or earlier is often still in excellent condition compared with machine-made paper manufactured during the last 150 years. Apart from so-called archive paper and alkaline fine paper with $CaCO_3$ as filler, most modern papers have a comparatively poor stability on ageing. In this context a brief historical review (Stuhrke 1977, Williams 1981, Smith 1969, Hunter 1978) can therefore be desirable.

Before the break-through of industrialism in the 19th century, paper was made by hand with primarily cotton and flax fibres as raw material. These papers were often sized by being dipped in gelatine, an Italian invention from the 14th century. The papers contained no fillers but often had an alkali reserve of a couple of per cent carbonate because of washing procedures used during the fibre preparation. In general these papers therefore have a good hydrolytic stability.

In 1774, when Scheele discovered chlorine, it was possible to start bleaching the raw material which could now also consist of coloured rags. These bleaching procedures exposed the cellulose to an oxidative attack with poorer ageing stability as a consequence.

In 1807, Moritz F. Illig invented the modern sizing procedure or more correctly hydrophobing procedure where resin soap is precipitated with alum. These papers, however, became acidic and the cellulose was exposed to a slow hydrolysis as it aged.

Paper made before 1870 was based mainly on linen and cotton rags, but the invention of the groundwood pulping process in 1858 and sulphite cooking in 1874 meant that wood could be used as raw material, but acidic sizing in combination with these early wood-based fibre types resulted in a paper with poor ageing stability.

In the beginning of the 20th century one began to understand that the acidity of the machine-made papers was the main reason for their poor ageing stability. In 1903, Winkler (Williams 1981) showed that paper which had been dipped in dilute acid disintegrated after a couple of years and these early techniques were summarized in some pioneer studies by Gösta Hall under guidance from Sigurd Köhler (Köhler and Hall 1925, 1926). Hall also initiated research activities at NBS (National Bureau of Standards, Washington) into the ageing stability of paper during his visit there in 1925 (Wilson 1983). He also introduced methods for the determination of methods for titratable acidity and accelerated ageing (72 h/100^{o}C) of which the latter is still today a Tappi-standard. Hall suggested that the addition of aluminium sulphate was the most important cause of hydrolysis during the ageing of paper.

The first documented paper manufactured from wood cellulose and stable during ageing was probably made in 1901 by Edwin Sutermeister at S.D. Warren. It was a calcium-carbonate-containing writing paper which in 1929 was found to be in excellent condition, in contrast to an acid-sized paper made from cotton rags. A consequence of this was that a many year long argument broke out as to whether it was the acid sizing or the raw material (wood cellulose compared with cotton) which was most important for the ageing stability.

The importance of acidity for accelerated ageing was documented at an early date (Williams 1981) and fold number was also established as a sensitive measuring parameter at a very early stage, Figure 1.1.

The great importance of air contamination was realized already in the 19th century and in 1931 Richter (Smith 1969) studied SO_2-absorption in paper and its effect on the acidity and breakdown of the paper.

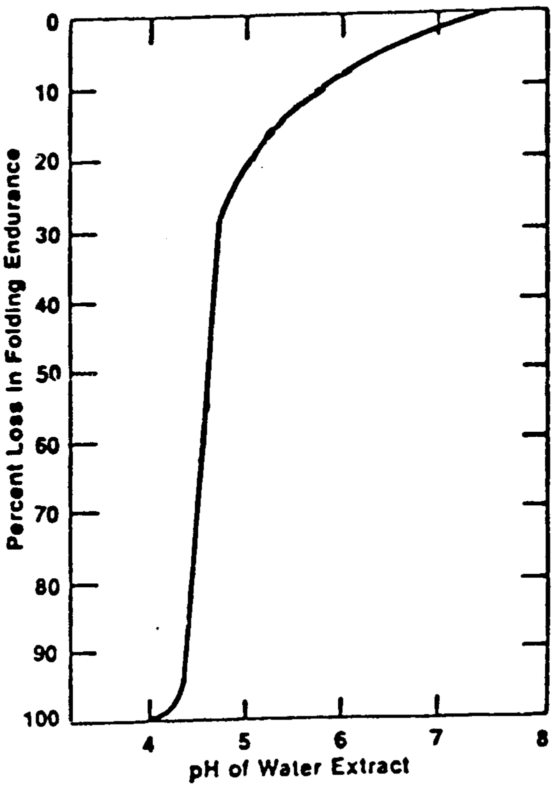

Fig. 1.1 The importance of acidity for accelerated ageing (Williams 1981).

The effect of temperature during accelerated ageing was studied in detail in the 1950s. The most definitive study by W.J. Barrow was published by the Virginia State Library in 1959 and 1960 (Barrow 1959, 1960).

W.J. Barrow studied the relationship between the breakdown during accelerated ageing and the acidity and he found that the acidity of the paper was of decisive importance for its stability. Shortly after the publishing of this report, several paper manufacturers also started to manufacture paper under alkaline conditions with calcium carbonate as filler. It should be observed that Barrow's studies were contemporary with the development of the first modern synthetic hydrophobing agents (so called alkyl ketene dimers (AKD)) which could be used in paper making under neutral or slightly alkaline (pH $\approx$ 8) conditions.

1b Effects of natural ageing on the properties of paper

Although the effects of ageing on the properties of paper, e.g. yellowing, brittleness etc are well known, there are extremely few studies in which the manufacturing conditions have been controlled and documented and the physical and chemical properties of the paper have been measured both during the manufacturing and after a longer period of storage. There is no study in which paper has been stored at room temperature over long periods of time (more than 20 years) under controlled conditions of temperature and humidity. It must also be observed that the measuring methods often become old-fashioned after a number of years and are replaced by modern methods. The literature is however rich in reports about what happens after accelerated ageing at e.g. 72 hours/dry climate/100°C (Tappi Standard).

The National Bureau of Standards (NBS) tested a number of commercial papers in 1929 and after 4, 8, 22 and 26 years of storage (Wilson et al 1955) which gave valuable data, but the manufacturing conditions for these papers where not documented.

In 1937 a number of papers were made on the NBS experimental paper machine under defined manufacturing conditions and these were tested and characterized carefully. (Shaw and O'Leary 1938).

These papers were tested again after 36 years of natural ageing ("office environment") by Wilson and Parks (1980) and some of their results are presented in tables 1.1 and 1.2 1.2. These data can be considered to be a representative selection and are primarily intended to illustrate some typical changes in properties.

It is generally known that the tensile index is a poor measure of ageing stability. It can further be observed that the fold number and tearing index are sensitive indicators of the ageing of paper. It is noteworthy that the paper made of cotton cellulose has also aged considerably, probably depending on the fact that it has been sized with aluminium sulphate and resin size.

Table 1.2 shows the change in α-cellulose content, R18 (content of insoluble cellulose in 18% NaOH), the Cu-number (a measure of the carbonyl group content) and extract pH during the ageing of paper. The table shows that α-cellulose content, Cu-number and extract pH are all sensitive markers of ageing in paper. A lower degree of polymerization (D.P.) of the cellulose implies a lower α-cellulose content. Oxidation attack (e.g. measured as Cu-number) also reduces the α-cellulose content because of alkaline hydrolysis during the measurement.

The extract pH decreases during storage because of oxidation (carboxyl groups), hydrolysis of aluminium salts and absorption of SO_2 and its oxidation product SO_3 (H_2SO_4). Together with D.P., fold number and tear index, the quantities in table 2 constitute classical measurement variables and indicators of cellulose degradation. Since the fold number plays a central role in investigations of embrittlement of paper, this variable is discussed in a separate chapter.

Table 1.1

Effect of 36 years natural ageing on some mechanical properties of paper (Wilson 1980)

Nr[1]	Fibre	Filler[2] content (%)	pH[3]	Alum additive (%)	Tensile index retention (%)	Stretch to failure retention (%)	Fold number retention (%)	Tear index retention (%)
1	*50% Si[4]/ 50% Sa[5]*	11	4.2	2.1	76	58	10	43
2	*100% alkali extract Si*	12	5.6	0.6	102	83	68	57
3	*Cotton*	14	4.9	1.3	98	95	78	67
4	*Cotton*	13.5	4.0	4.0	101	78	56	57

1) Refers to papers 1129, 1164, 1192 and 1203 (Wilson 1980)
2) Kaolin
3) pH in headbox position during the manufacture
4) Sulphite pulp
5) Kraft pulp

Table 1.2

Effect of 36 years natural ageing on some papers and their chemical characteristics (Wilson 1980)

Nr[1])	Fibre	pH	α-cellulose content (%)	Cu-number 1937	Cu-number 1973	Extract pH (cold) 1937	Extract pH (cold) 1973
1	50% Sulphite/ 50% Kraft	4.2	-16.7	3.6	4.8	4.9	4.5
2	100% alkali extract sulphite	5.6	- 4.0	0.9	1.7	6.0	5.0
3	Cotton	4.9	- 8.0	0.4	1.1	5.8	5.1
4	Cotton	4.0	-16.5	0.7	2.3	5.3	4.8

1) Refers to papers 1129, 1164, 1192 and 1203 (Wilson 1980).

It is further well known that the brightness of paper decreases during ageing, but studies of its variation during natural ageing over longer periods of time are lacking. This depends partly on the fact that the modern optical measuring methods and the so-called Kubelka-Munk theory (Kubelka 1948), where the optical properties are separated into a k-value (light absorption coefficient) and an s-value (light scattering coefficient) have not been in use for long. It is known that the s-value does not change during accelerated ageing and there are theoretical reasons for assuming that this is also the case during natural ageing (Luner 1969). This means that the bonded area in paper does not change during ageing.

An analysis by Page (1969) shows that it is primarily the fibre strength which decreases during accelerated ageing while the fibre bonding strength instead increases. Since the fibre bonding strength increases but not the bonded area and the wet strength increases (Graminski 1970) during both natural and accelerated ageing there are strong reasons for believing that covalent bonds (cross-links) are formed between the fibres during ageing. (See further chapter 3c).

It has also been established that the specific modulus of paper increases during natural ageing (Graminski 1970). Since the specific modulus for polymer materials usually decreases with decreasing molecular weight (Alfrey 1948), this suggests that other physical and chemical processes take place simultaneously. These can be a relaxation of the free volume (see chapter 5), crystallization of the cellulose as a result of hydrolysis (see chapter 3d) or cross-linking (see chapter 3c). All these phenomena are discussed under separate headings. The dimensional stability of paper is also improved (the hygroexpansion decreases) during ageing, which can be related to the effects mentioned (Luner 1969).

1c Survey of decomposition and ageing mechanisms of cellulose

The degradation and ageing mechanisms of cellulose can be roughly subdivided in the following way: (Wilson 1979, McBurney 1954).

1. Chemical degradation mechanisms

   a) Hydrolysis. The degree of polymerization of the cellulose is reduced and reducing free end-groups are formed.

   b) Oxidation. The degree of polymerization of the cellulose is reduced and carboxyl groups (aldehydes and ketones) are formed.

c) Cross-linking. Cross-links are formed between the cellulose chains with e.g. semi-acetal bonds.

d) Microbiological breakdown. The degree of polymerization of the cellulose is reduced.

e) Mechano-chemical breakdown. The degree of polymerization of the cellulose decreases through chain-cleavage and mechano-chemical (stress-induced) oxidation.

2. Physical ageing mechanisms

a) Crystallization. Changes in the state of order of the cellulose induced through hydrolysis.

b) Relaxation of the free volume of the cellulose in the amorphous parts of the polymer.

Hydrolytic degradation has historically (Wilson 1979, Wessel 1970, Wilson 1983, Williams 1981, Smith 1969) been looked upon as the most important reason for the breakdown of cellulose during the ageing of paper. What is important in this context is that the degradation processes are often very strongly related, both the acid and the oxidation hydrolysis. The rate of hydrolysis of cellulose thus increases strongly when it is oxidized. Acid hydrolysis leads similarly to the forming of reducing end-groups which can easily be oxidized to carboxyl groups, which induce autohydrolytic breakdown of the cellulose. Hemicellulose is hydrolysed more rapidly than cellulose and acidic degradation products which are formed accelerate the hydrolysis. A higher content of non-cellulosic material in the fibre leads to a higher content of carboxyl groups, which can act autohydrolytically depending on the ionic form in which they exist.

If one starts from a fibre material with a higher content of carboxyl groups, this leads to an increased content of transition metals in the paper, because of the ion exchange with the acidic groups, and these transition metals (Fe, Mn etc) catalyse oxidation processes including the oxidation of sorbed SO_2 to H_2SO_4 (from environmental contamination).

Oxidation bleaching, by e.g. Cl_2, hypochlorite or oxygen is harmful because of the fact that the carboxyl content increases. The formation of chlorinated residual products (chlorinated lignin, chlorinated extractive substances) in the fibre during chlorine-based pulp bleaching makes possible the formation of HCl and a subsequent hydrolytic attack.

Cross-linking of the cellulose through the formation of e.g. hemiacetal bonds (acid catalysed reaction) has an embrittling effect as does crystallization (induced through hydrolysis) or relaxation of the free volume of the amorphous cellulose (natural physical ageing of polymers).

Photochemical degradation is in general of less importance for books which are stored in the dark in a library, but photo-sensitized oxidation can otherwise be an important breakdown process.

An increase in moisture content or in temperature increases the rates of both hydrolytic and oxidation degradation processes and also the crystallization and relaxation processes.

Cyclic variations in the moisture content (or indirectly through a changed temperature) accelerate the ageing processes still more. The breakdown and ageing of a paper therefore depends in a complex way on the chemical environment, the composition of the raw material etc. and can therefore in principle not be predicted from kinetic investigations (Arrhenius-extrapolation) unless the ageing process is completely dominated by a single degradation process, e.g. acid hydrolysis. This seems nevertheless to have been the case since a correlation still seems to exist between accelerated and natural ageing (Wilson 1980).

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2 FOLD NUMBER AND FOLDING ENDURANCE
- An analysis of test methods

In its daily use, paper is exposed to repeated foldings and wrinklings and its ability to resist such stresses is one of its most important quality criteria. Different apparatuses have been constructed in order to test this property, in which a paper strip is quickly folded backwards and forwards under a certain applied tensile stress until it breaks.

The fold number is the number of double folds that are required in order to cause failure of a test strip. A double fold is a complete folding cycle during which the test piece is first folded backwards and then forwards along the same folding line.

The folding endurance is the common logarithm of the number of double folds.

The folding endurance is an empirical strength measurement originally developed in order to characterize paper which was exposed to folding during use.

Bearing in mind the original purpose of the measurement, it is really incorrect to perform the determination with an applied tensile stress, since the paper in practice is seldom exposed to a tensile stress at the same time as it is folded or wrinkled.

Besides the fact that the measurement of folding endurance does not quite correspond to its original purpose, the long testing time for strong papers and above all the considerable scatter of the test results should be mentioned as disadvantages of the method.

The deviation is caused mainly by the heterogeneity of the paper; the area which is folded is rather small and local structural variations in the paper have a considerable effect on the result.

Folding endurance is however more sensitive to changes in the structural properties of the paper than any other strength measurement. For this reason, the determination is often included in routine measurements during the testing of paper and pulp. As an example of the sensitivity of the folding endurance to structural changes in the paper, its use in different ageing tests can be mentioned.

This chapter describes in principle different apparatuses which can be found on the market and discusses the effects of different test variables.

2a Test methods

Different apparatuses are available for the testing of folding endurance. ISO-5626 describes the use of four different apparatuses which however do not necessarily give the same result. Most other standards describe the use of one or more of these apparatuses.

a) The Schopper instrument

The principle of the Schopper instrument is shown in figure 2.1. Strips with a width of 15 ± 0.02 mm and a length of 100 mm are used for the test.

The strips are held in a pair of horizontally opposed clamps with spring loading which varies during the folding cycle.

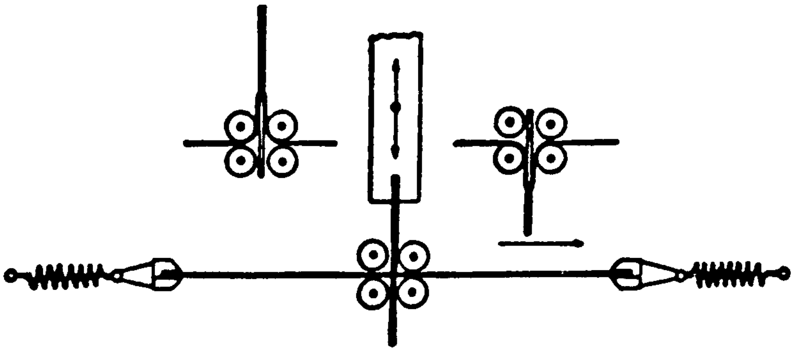

Figure 2.1 The principle of the Schopper-instrument, seen from above.

The folding is achieved by placing the middle of the strip in a vertical slot in a blade which goes up and down between four rollers which are symmetrically arranged around the slot in the reciprocating blade when this is in its middle position.

When the clamps are furthest from each other, each spring exerts a pull of 7.55 N ± 0.10 N, and, when they are closest to each other, 9.81 N ± 0.10 N. The instrument makes 110 ± 10 double folds/min.

The length of the stroke of the folding blade is 20 mm. The thickness of the folding blade is 0.5 mm and its edges are cylindrical with a radius of 0.25 mm.

b) The Lhomargy instrument

The principle of the Lhomargy instrument is similar to that of the Schopper instrument. Instead of the horizontally opposed spring-loaded clamps in the Schopper apparatus, the test strip in the Lhomargy instrument is loaded with a dead weight of either 4.91, 8.68 or 9.81 N, where 8.68 N is intended to give the same mean loading as that on the Schopper instrument. The instrument makes 125 ± 5 double folds/min with a 20 mm stroke length.

c) The Köhler - Molin instrument

The principle of the Köhler - Molin instrument is shown in figure 2.2. It embodies two folding units, each consisting of an upper folding clamp and a lower loading clamp, in which two test strips can be fastened and tested at the same time.

From a vertical starting point, the folding clamp oscillates 156 ± 2° in each direction. The folding rate is 200 ± 10 double folds/min. The loading clamp can be equipped with weights and the total load on the test strip shall be 7.85 ± 0.02 N.

The distance between the upper edge of the loading clamp and the rotation axis of the folding clamp during the test is 62 ± 1 mm. When the test piece has broken, the loading clamp falls down against a stop. The radius of the edge of the clamp in contact with the paper shall be 0.25 mm. The pivot point of the jaw shall be 0.04 mm from the edge of the fixed jaw of the clamp.

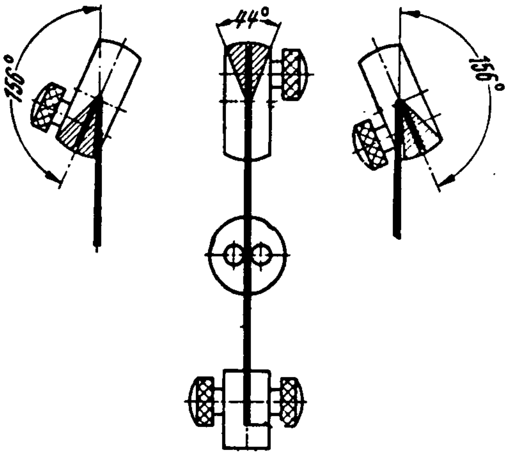

Figure 2.2 The principle of the Köhler–Molin instrument

d) The MIT instrument

The MIT instrument, shown schematically in figure 2.3, consists of a clamp which can move vertically over a folding head, 60 mm below its tip. The strip is loaded with a load of between 4.91 and 14.72 N.

The surfaces forming the slot in the folding head have a radius of 0.38 ± 0.02 mm. The clamp oscillates with 175 ± 10 double folds/min through an angle of 135 ± 2° in each direction.

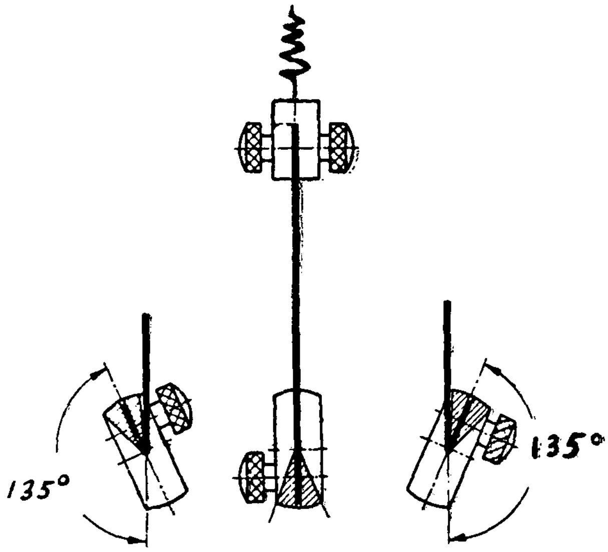

Figure 2.3 The principle of the MIT instrument.

2b Analysis of the folding process

During the measurement of folding endurance the test strip is exposed to tensile, bending and shearing stresses. When the test strip is bent its outer surface is stretched and its inner surface compressed to an increasingly greater extent the sharper the bending radius is and the thicker the paper sample is. One realizes therefore that the folding endurance depends not only on the tensile strength of the paper but also on its compression strength, elasticity modulus and stretchability. The behaviour of the paper during the folding endurance measurement can be visualized by studying the stress distribution in a strip in the straight or bent state in the following way.

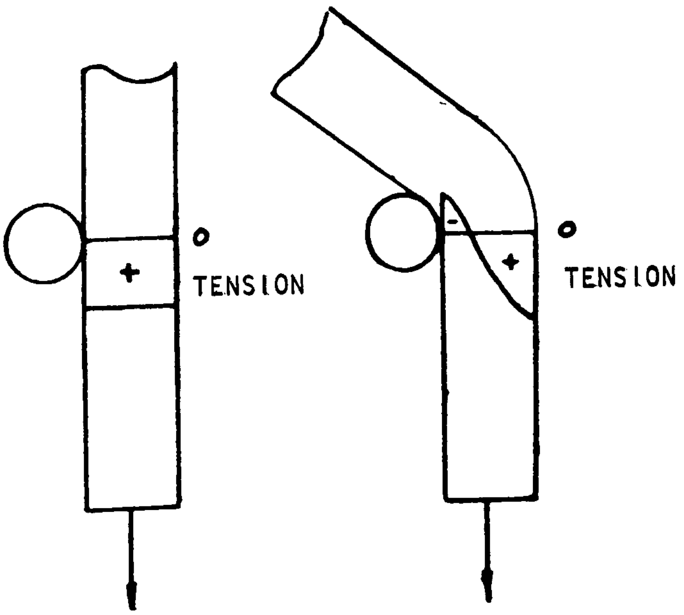

Figure 2.4 Stress distribution in a) a straight paper strip and b) a bent strip.

Depending on the test method, the strip will be more or less loaded in the straight state during the initial phase. The stress distribution is uniform. In the bent state the bending stress is superimposed so that the stress decreases on the concave side and increases on the convex side. Delaminating shear stresses are also added. Depending on the grammage and stiffness of the paper, a standardized load will have a different effect on the paper in the straight state from negligible elastic strain to strain to failure. In unfortunate cases the paper breaks before the measurement has started (Goldberger, Rhyne 1966).

When a strip is bent over a radius of R = 0.25 mm (Köhler-Mohlin), the strain is theoretically $\varepsilon = t/R$ where t is the thickness. For a sheet with a thickness of 0.1 mm, the strain is theoretically 40% and for 0.2 mm 80%, i.e. far above the limit to failure (Goldberger, Rhyne 1966). Because of edge effects, compression failure and shearing, the strain is however in reality smaller.

The example shows that strong and thin papers are fatigued least during folding testing, whereas weak and thick papers are fatigued more quickly.

The failure process will thus take place as illustrated in figure 2.5. In the beginning stage, the strip is more or less tensile loaded a). Under a small bending force b) the inside is compressed and the outside is stretched, the net stresses probably always being in tension.

With increasing bending c) compression failure can take place on the inside, which causes local delamination, as is illustrated in figure 2.6 for cartonboard (Carlsson, Fellers 1980).

At the same time, under large bending stresses, some surface fibres break on the outside of the sheet in tension. Under repeated bending d), the effective thickness is reduced through surface failure and the bending stresses become smaller. The tensile stresses increase on the other hand. The strip can still withstand the applied tensile force.

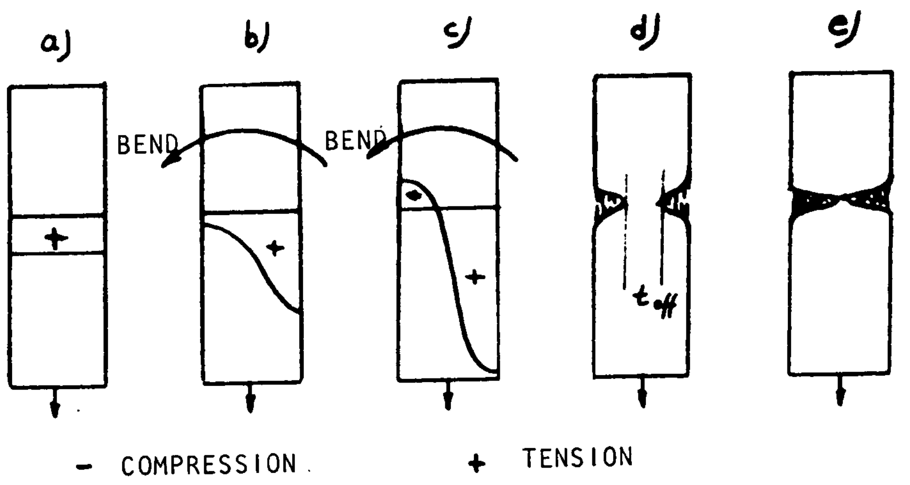

Figure 2.5 Stress distribution during different stages of the folding process.

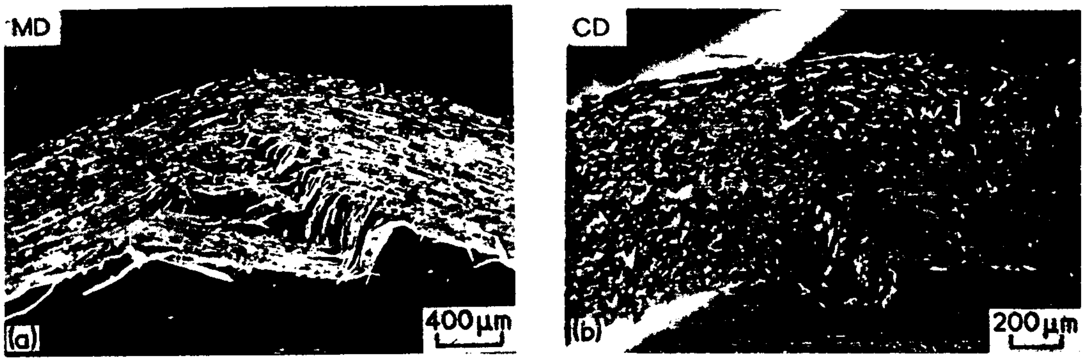

Figure 2.6 SEM pictures of the edge of a paper exposed to bending (Carlsson, Fellers 1980).

Eventually e) the remaining area is so small that the strip can no longer resist the applied tensile force.

2c Influence of different variables

The folding endurance is affected by apparatus parameters, paper technology variables and the testing climate. The influence of the most important parameter is here summarized.

a) Folding angle

The folding endurance decreases with increasing folding angle. In the Köhler-Mohlin apparatus, for example, the normal folding angle in one direction is 156°. If the angle is reduced to 135°, the fold number increases 2.3 % per degree. If the angle is reduced further, down to 104°, the fold number increases with 4 % for every reduced degree compared with the fold number determined with a folding angle of 156° (Köhler 1956). The different folding angles are one of the reasons why the different apparatuses do not give comparable results.

b) Radius at the clamp

With a smaller radius of curvature, a lower folding endurance is obtained because greater bending stresses are introduced (Köhler 1956).

c) Load

If the determination of folding endurance is interpreted as a tensile test performed on a paper exposed to stresses in the form of foldings, it is easy to draw the conclusion that the tensile stress required to break the test strip becomes smaller the more the paper has been folded or conversely that the folding endurance diminishes the greater the tensile stress to which the test strip is exposed during the determination.

Cardwell et al (1972) established a relationship between load L and the number of double foldings F according to:

$$\ln F = m L + b$$

where m and b are constants. Figure 2.7 shows some results.

Alternative equations have been suggested (Luner 1973).

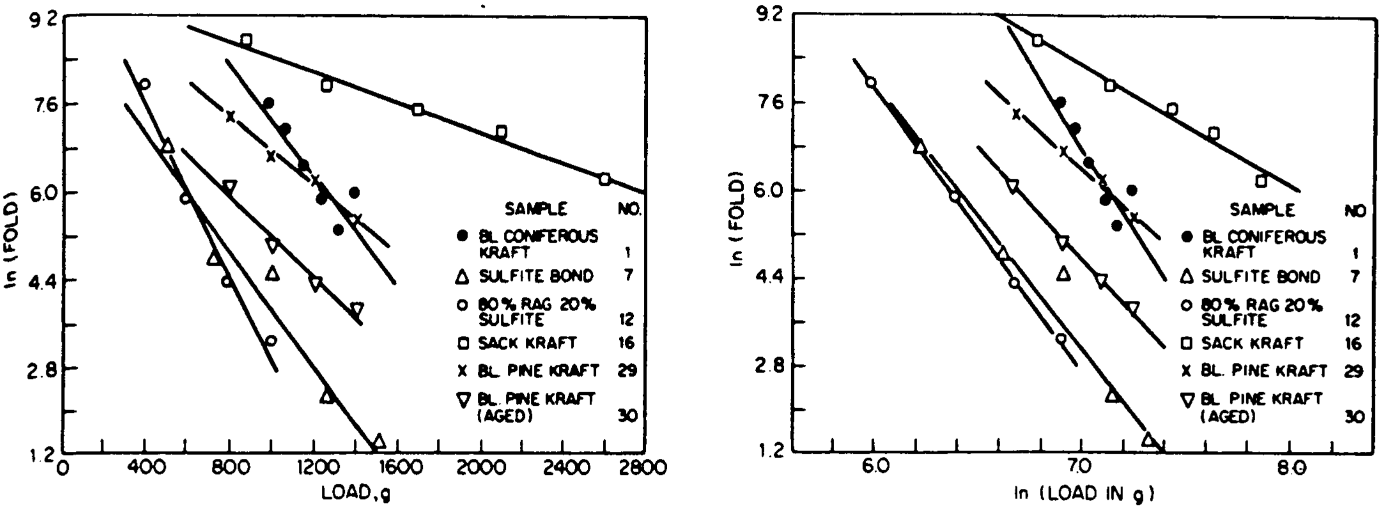

Figure 2.7 Natural logarithm of fold number against load. (Cardwell et al 1972).

During measurement of the folding endurance, a standardized load is in general used. The fact that the same load is used for completely different papers means that paper with a low tensile strength, e.g. thin paper grades, often end up in an unfavourable position, since the applied load for these weak papers constitutes a greater fraction of the paper's tensile strength than is the case for thicker paper grades.

The equation offers the possibility of comparing folding endurance under other loads than that which is standardized.

d) Grammage

The folding endurance of papers manufactured from the same pulp increases with increasing grammage to a maximum value and then decreases. The tensile strength of the test strip increases with increasing grammage, but at the same time the thickness of the paper increases with higher bending stresses as a result. For thin and weak papers, the tensile strength increase is a more decisive factor than the increase in bending stress. This means that the folding endurance at first increases with increasing grammage. Finally a point is still reached, where the bending stress is more decisive than the growth in tensile strength and the fold number begins to decrease. This relationship is illustrated in fig. 2.8 (Brandon 1966).

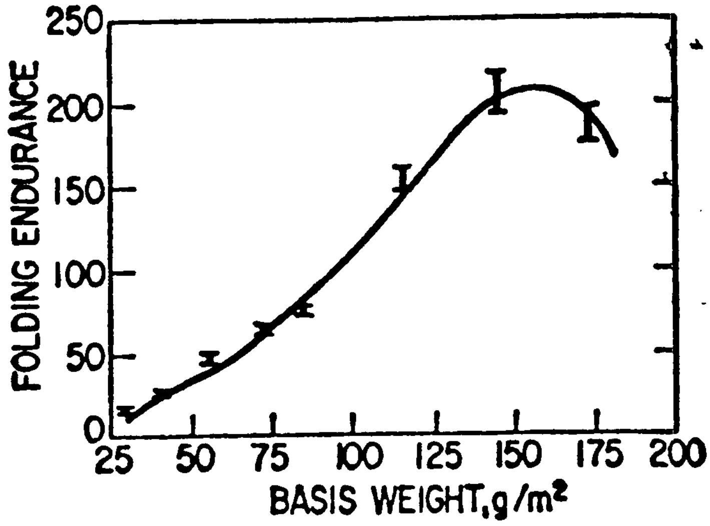

Figure 2.8 Fold number against grammage for hardwood pulp beaten for 20 min. (Brandon 1966).

The results show that it is often the bending stresses which are the most serious for the fatigue process (Köhler 1965).

A suggestion that the load should be set in proportion to the tensile strength of the strip will therefore only marginally improve the comparison (Köhler 1965).

The sensitivity to the load on strips of a given pulp decreases with increasing grammage as shown in figure 2.9 (Goldberger, Rhyne 1966).

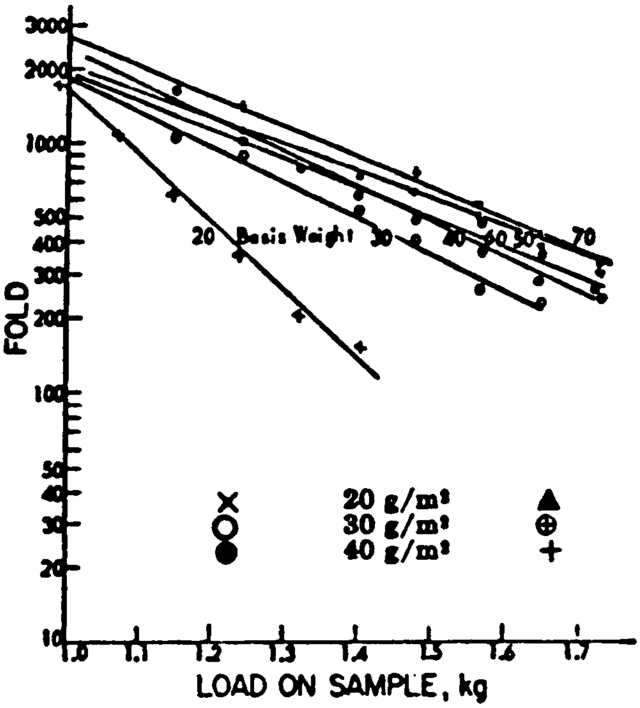

Figure 2.9 Fold number against load at different grammages (Goldberger, Rhyne 1966).

e) Fibre orientation

The folding endurance, when testing according to the standard procedure, is in general greater in the MD (machine direction) than in the CD (cross-direction) (Köhler 1956).

If the folding endurance is measured so that the tensile stress on the test strip is the same fraction of the paper's tensile strength, however, the folding endurance in the CD is always greater than that in the MD (Köhler 1956). This probably depends on the fact that the extensibility is greater in the CD. Greater shrinking during drying should thus favour the folding endurance. The sensitivity of the folding endurance to load is greater for CD samples according to figure 2.10 (Goldberger, Rhyne 1966).

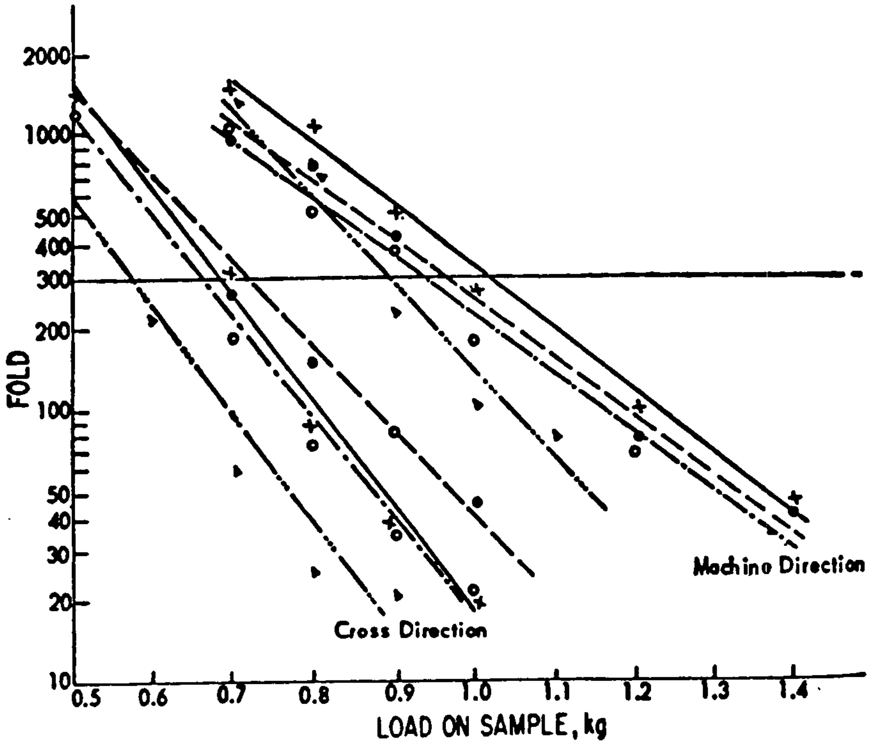

Figure 2.10 Fold number against load in the MD and the CD. (Goldberger, Rhyne 1966).

f) The temperature and relative humidity of the air

With increasing relative atmospheric humidity, the moisture content of the paper also increases. An increasing moisture content in the paper causes the tensile strength and stiffness to decrease, while the extensibility increases. The folding endurance increases quickly with increasing moisture content, in spite of the reduced tensile strength. The increase can be assigned to an increased extensibility and increased toughness of the fibres.

The temperature affects the folding endurance indirectly, since the relative humidity of the air varies with the temperature of the air. If the temperature in the folding point is higher than that in the conditioned test room, the relative humidity of the air decreases in the folding zone and the measurement gives too low a value.

Since the folding endurance is very climate dependent, temperature and humidity variations should be kept to a minimum. In practice, it has become apparent that one can reduce the scatter of the fold number considerably by preventing the motor of the apparatus from heating the air close to the test strip (Kahlson, Lindholm 1956; Kahlson, Mårtensson 1964).

g) The influence of the sheet structure

The structure of the paper is of great importance for the folding endurance. In one trial (Bristow, Pauler 1983), three-layer sheets with different layer compositions were manufactured from chemical and mechanical pulp. Figure 2.11 shows the results.

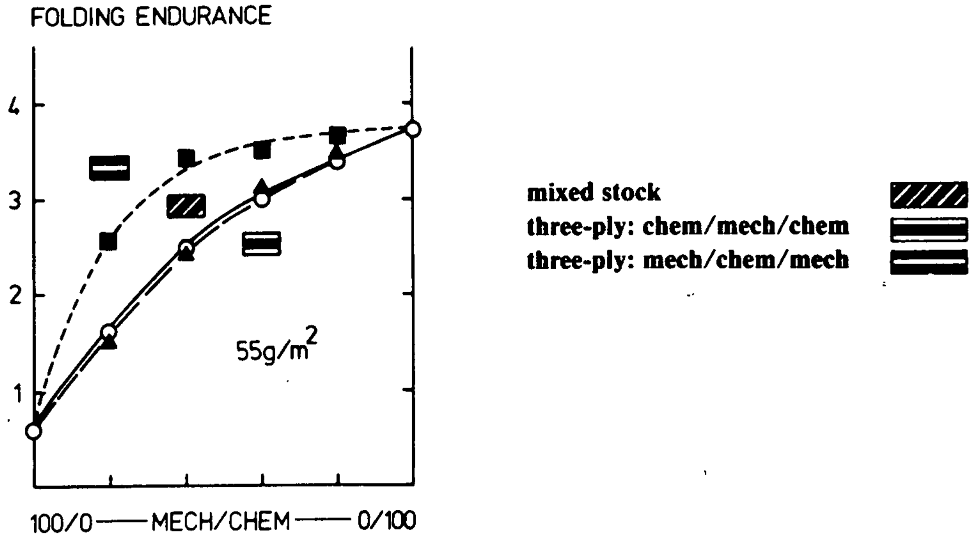

Figure 2.11 The folding endurance versus composition for layered and mixed structures with different proportions of groundwood and chemical pulp at 55 g/m² (200g load) (Bristow, Pauler, 1983)

The highest folding endurance was obtained when mechanical pulps were placed outermost, the reason being that although the mechanical layers may break quickly the middle layer of chemical pulp remained whole in a further number of foldings.

According to figure 2.12 the folding endurance increased with increased grammage. The two-sidedness in the paper causes the fatigue to become different on the two sides of the sheet.

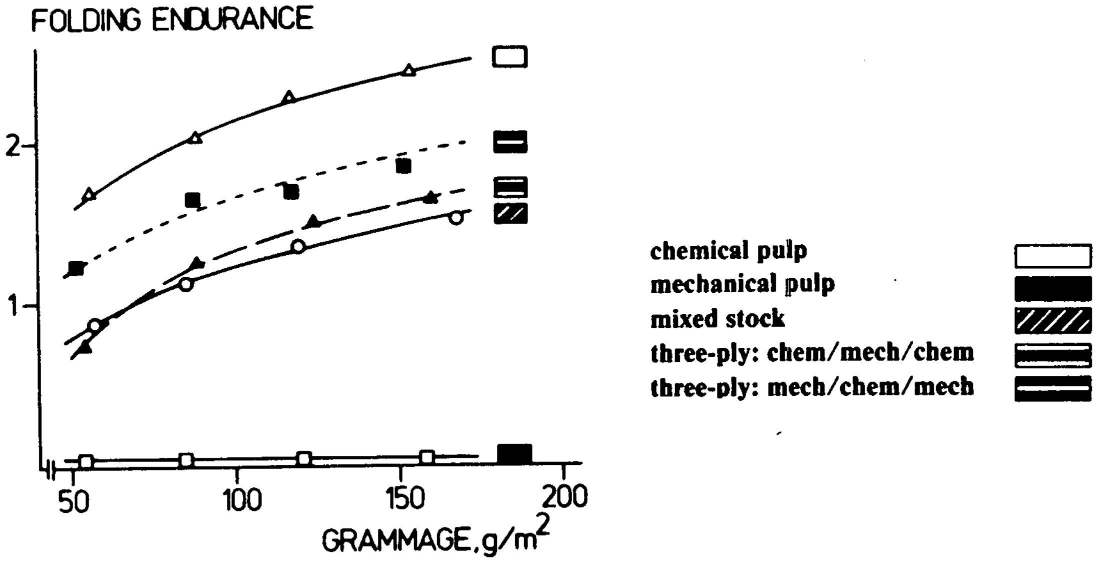

Figure 2.12 *The folding endurance versus grammage for layered and mixed structures of groundwood and chemical pulp (800 g load)*
(Bristow, Pauler, 1983)

Conclusions

The folding endurance is an empirical strength measurement which was originally developed for characterizing paper which in the final use is exposed to folding.

Bearing in mind the purpose of the measurement, it is in reality incorrect to carry out the determination with an applied tensile stress, since the paper in practice is seldom exposed to a tensile stress at the same time as it is folded or wrinkled.

Suggestion for alternative comparison of different papers

On the basis of the above mentioned effects, Köhler suggested in 1956 that the residual tensile strength as a percentage of the original strength should be measured after 1000 double folds under a load equal to 5% of the mean tensile strength.

The folding endurance is more sensitive to changes in the structural properties of the paper than any other known strength measurement. For this reason, the determination is often included in routine measurements during the testing of paper and pulp. As an example of the sensitivity of the folding endurance to structural changes in the paper one can mention its use during different ageing tests.

In addition to the fact that the measurement of folding endurance does not quite correspond to its original purpose, the long test time necessary for strong papers and above all the large scatter of the test results deserve to be mentioned as disadvantages of the method.

The scatter is caused mainly by the heterogeneity of the paper; the area which is folded is rather small and local structural variations in the paper strongly affect the result.

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3 CHEMICAL REACTIONS DURING NATURAL AND ACCELERATED AGEING

3a Acid hydrolysis of the polysaccharide components of the paper

The glucosidic bonds of the polysaccharides (acetal bonds) are stable in neutral and moderately alkaline environments, disregarding possible oxidation reactions. In an acid environment, however, the bonds are hydrolysed, the speed increasing with increasing hydrogen ion activity (Sharples 1971), and the molecular weight (the degree of polymerisation - DP) of the polysaccharides decreases. The polysaccharides in pulp fibres can be roughly divided into two groups according to their reactivities. One is made up of hemicelluloses and the other of cellulose.

Hemicelluloses

The structure and relative occurrence of the hemicelluloses varies between different species of tree. In a pulp technological context they can however be divided up into glucuronoxylans and glucomannans. There are also other type of wood polysaccharides but the amounts of these in pulp fibres are relatively small, and they are therefore ignored. The hemicelluloses are readily hydrolysed because of their strongly amorphous character, although the order (crystallinity) can increase somewhat during chemical pulp production (Rydholm 1965). Besides such supramolecular effects, model studies show that the glucosidic bonds in glucomannans (β(1-4)-mannosidic) and glucuronoxylans (β(1-4)-xylosidic) have 6 to 10 times higher reactivity than cellulose bonds (Overend 1972). Glucuronoxylan is also an acidic polysaccharide, containing glucuronic acid groups, which increases the possibility of autohydrolysis.

Cellulose

Analysis of the reactions which take place during heterogeneous hydrolysis of cellulose are complicated by the fact that the cellulose in the fibres (there are no paper fibres) can have a varying degree of crystallinity and can also occur in different crystal forms (so-called polymorphous substances). In a simplified way, the cellulose fibres can be said to be built up of segments of anhydro-glucose units with different conformations, even though there is still an open debate about what these in reality look like (Atalla 1987). Native cellulose and ordinary pulp fibres consist mainly of amorphous (non-crystalline) cellulose and crystalline cellulose I. The proportions vary depending on the origin and treatment of the fibres. Other types of crystalline cellulose, so-called cellulose II, may also occur in small amounts. Although these factors will affect the heterogeneous cellulose hydrolysis, the process can be treated as first order reactions which follow ordinary kinetic laws. The following two rate equations can therefore be used to describe the hydrolysis (Feller 1984).

$$\ln(1 - 1/Dpn,o) - \ln(1 - 1/Dpn,t) = k \cdot t \qquad (1)$$

where Dpn,o and Dpn,t are the numerical mean values for the degree of polymerisation at time 0 and time t respectively. At a low degree of hydrolysis, i.e. when only a small proportion of the bonds have been broken, the equation can be simplified to

$$1/Dpn,t - 1/Dpn,o = \alpha \cdot k \cdot t \qquad (2)$$

where the factor α is a measurement of the accessibility of the bonds and k is the velocity constant for hydrolysis of normal β(1-4)-glucosidic bonds, i.e. supramolecular effects are included not in k but in α.

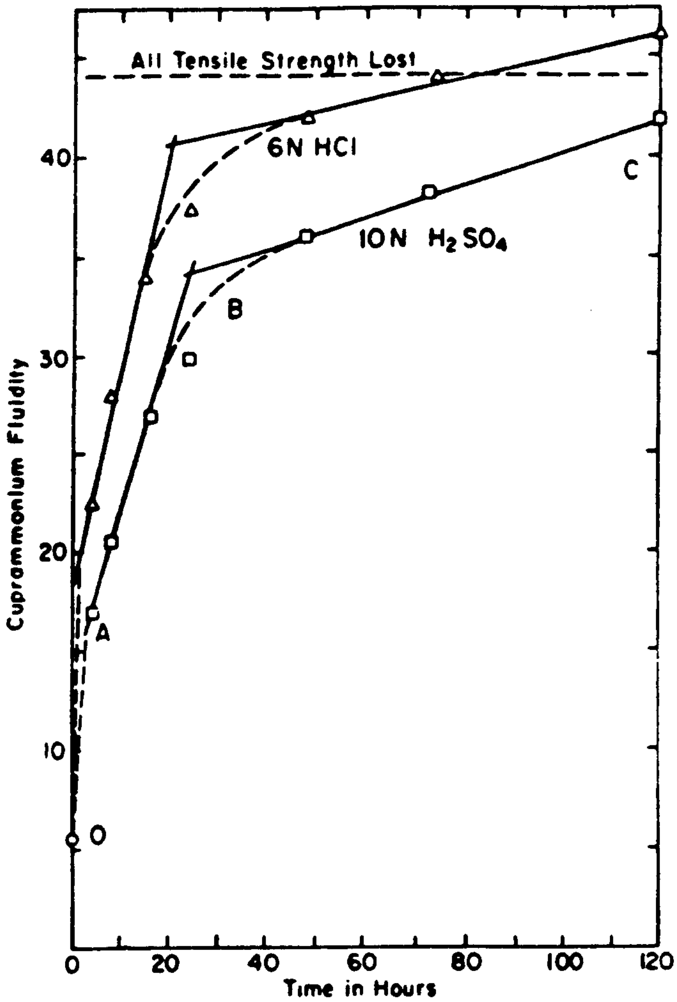


Figure 3.1 Change in cuprammonium fluidity during acid hydrolysis of cotton cellulose (Davidson 1943).

Results of acid hydrolysis of cotton cellulose at 20°C are shown in figure 3.1. The increase in fluidity (the inverse viscosity which is proportional to 1/Dp) with time indicates that there are three different stages in the hydrolysis, i.e. three different accessibility factors α. There is an initial very fast hydrolysis (0 to A), which changes between A and B to a more normal hydrolysis rate for the β(1-4)-bond and finally from B to C there is a very slow hydrolysis. These three different stages are explained by supramolecular effects in the organization of the cellulose molecules, since the bonds to be hydrolysed are chemically identical, i.e. β(1-4)-glucosidic.

Initial phase (0 to A): The relative rate of hydrolysis is up to 10 000 times higher than for normal β(1-4)-bonds. An explanation which has been investigated is the possible occurrence of oxidized anhydroglucose units, but glucosidic bonds to such units are hydrolysed only about 100 times faster (Daruwalla 1966). It is assumed instead that purely physically induced stresses cause these high breakdown rates.

Normal hydrolysis (A to B): In this stage, hydrolysis of glucosidic bonds takes place in the amorphous cellulose zone. The rate agrees well with the hydrolysis of normal β(1-4)-bonds with a certain correction for the accessibility in the fibres.

Final phase (B to C): Only crystalline cellulose remains and the so called LODP-value (levelling-off DP) which corresponds to a DP of 150-200 has been attained. The hydrolysis takes place mainly on the surface of cellulose crystals, thereof the low rate. The strength of the paper (the fibre) has completely disappeared.

3b Oxidative decomposition of the polysaccharide components of the paper

For cellulose, and other wood polysaccharides, to oxidize during the ageing, access to an oxidation agent is required, Under strongly alkaline conditions (Entwistle 1949) or at high temperatures, the oxygen of the air can react directly with cellulose, If cotton linters are heated in an oxygen atmosphere (170°C) a rapid degradation of the amorphous cellulose takes place until the LODP has been attained. Thereafter the breakdown continues at a considerably slower rate. In an inert nitrogen gas atmosphere, only a slow reaction takes place under the same temperature conditions (Major 1958, Blazej 1985).

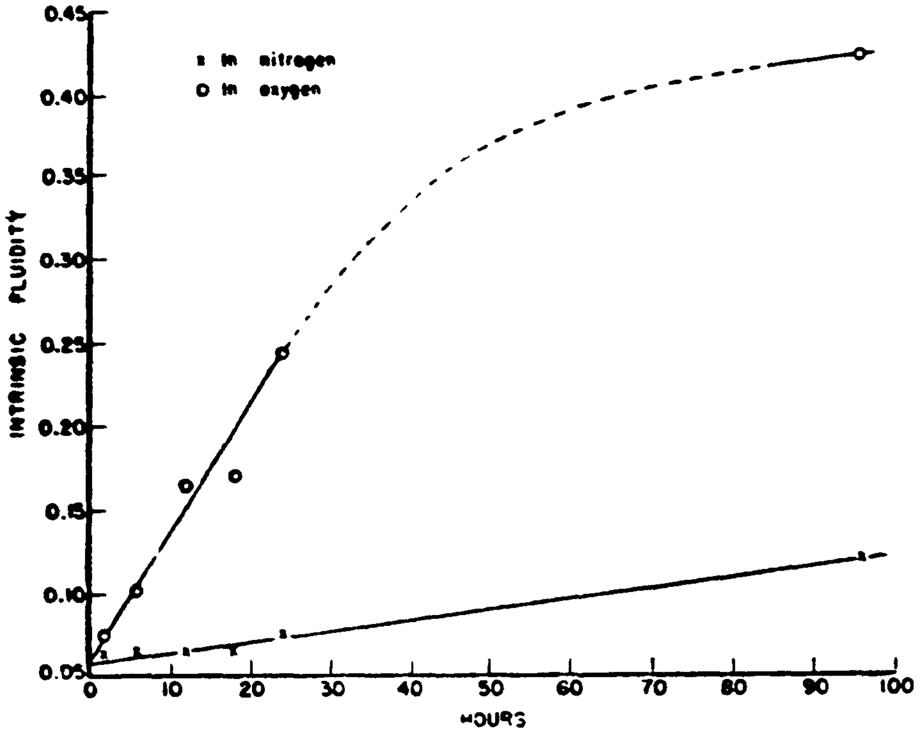


Figure 3.2 Change in fluidity during chemical ageing (170°C) of cellulose in oxygen or nitrogen (Major 1958).

The autoxidation of cellulose (polysaccharides) in air at normal temperatures and pH-values is scantily described in the literature. Marraccini and Kleinert (1962, 1963, 1966) have however shown that peroxides are formed during the ageing of bleached chemical pulp already at temperatures below 100°C. Possible functional groups which can be autoxidized under these milder conditions are reducing carbohydrate end-groups or carbonyl groups which have been introduced along the polysaccharide chains during the pulp bleaching. Residues of lignin and extractive substances with different unsaturated groups in the pulp may also participate in formation of peroxide during autoxidation. During the hydrolytic degradation of cellulose, new low molecular products (Rapson 1964, Schurz 1963) are formed which can increase the paper's sensitivity to oxidation. This means that the oxidation breakdown of paper can have a greater importance the farther the hydrolytic ageing process has reached.

The peroxides formed are very strong oxidation agents and decompose homolytically giving different radicals especially in the presence of certain heavy metals (see section 7c), at higher temperatures or under light irradiation. These radicals, regardless of whether they are derived from cellulose or other paper components, can then initiate the breakdown of polysaccharide chains. A single radical can oxidize e.g. several anhydro-glucose units on the cellulose chains by so-called chain reactions. The chain reactions depend on the fact that radical reactions have low activation energies, which causes the new cellulose radicals formed in the reaction to react further in so-called propagation steps until the reaction chain is completed by the formation of a very stable radical (i.e. phenoxy radical) or a combination of two radicals ($2R\cdot \rightarrow R-R$) in a so-called termination step. The radical reactions can introduce carbonyl groups along cellulose chains (C-6-, C-3- and C-2-positions) and make the cellulose sensitive to chain cleavage by so-called β-elimination in a second stage.

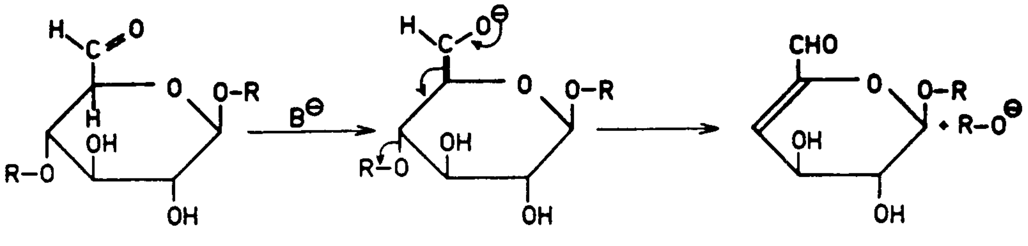


Figure 3.3 β-elimination (chain cleavage) of cellulose at a 6-aldehydro unit.

The β-elimination takes place fairly easily over the whole pH-interval but is especially rapid under alkaline conditions (Theander 1958, Luetzow 1974). This means that even a mild alkaline treatment of an oxidized pulp can cause a decrease in the degree of polymerization of the cellulose. The radical reactions can also cause direct chain cleavage in polysaccharides which is exemplified for a C-1-radical in cellulose in figure 3.4.

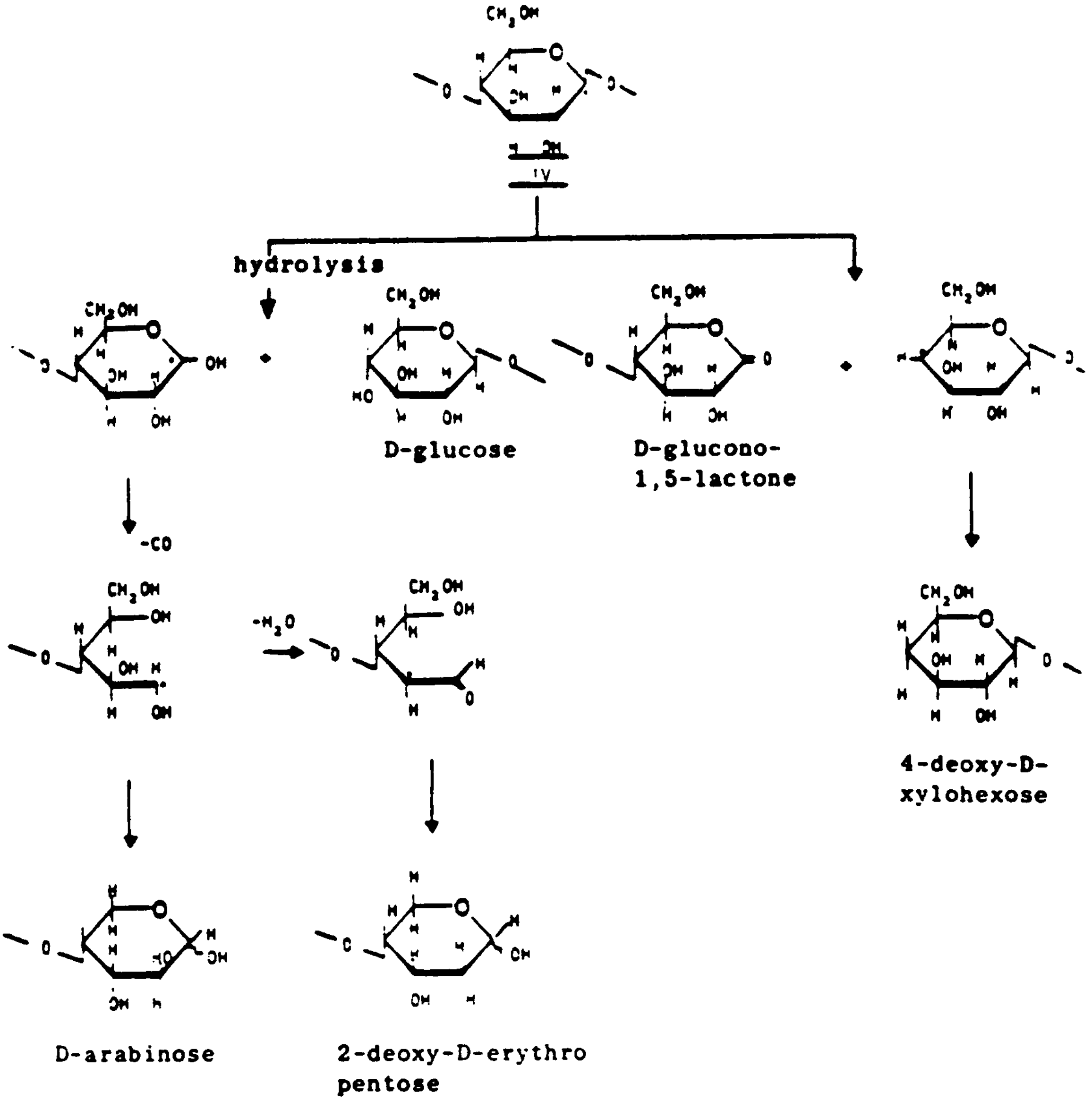


Figure 3.4 Reaction processes induced by radical formation at the anomeric centre (C-1) in cellulose.

The radical reactions are extremely complex processes and are therefore not fully described in this summary. Instead, two excellent survey articles by Sonntag (1980) and Philipp (1985) are recommended.

These examples show that the autoxidation decomposition of cellulose is of great importance for the ageing of the paper. The autoxidation, however, also introduces acid carboxyl groups into the different components of the paper, which means that oxidation can accelerate the hydrolytic degradation of the cellulose.

3c Crosslinking reactions

It is well known that when paper is exposed to heat in an accelerated ageing test the light scattering ability of the sheet is not changed (Tongren, 1938). This means that the bonded area of the sheet is unchanged after the heat treatment.

Page (1969) has also shown that the fibre bonding strength of paper increases during heat treatment whereas the fibre strength decreases. These results also agree with the fact that the wet strength of paper increases during heat treatment (Stamm 1959, Back 1967). The wet strength can increase up to 40% of the dry strength of the paper (Luner 1969). Figure 3.5 shows how heat ageing at 80°C and 81% RH affects the wet strength (Luner 1973).

Graminski (1970) has also shown that the wet strength of paper increases during natural ageing, and it is probable that it is a matter of similar mechanisms. The wet strength increase is assumed to depend on crosslinking in the cellulose wall of the fibres and in the fibre-fibre bonding surfaces.

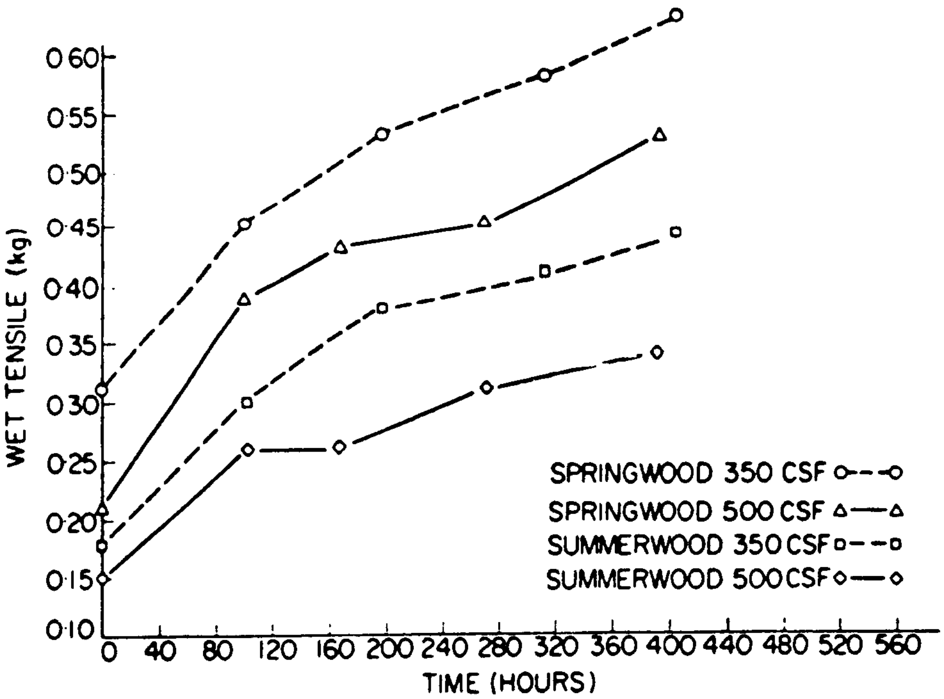
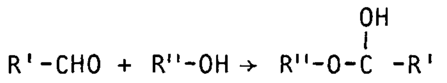


Figure 3.5 Effect of thermal ageing at 80°C and 81% RH on the wet tensile strength of paper manufactured from summerwood or springwood fibres. (Luner 1973)

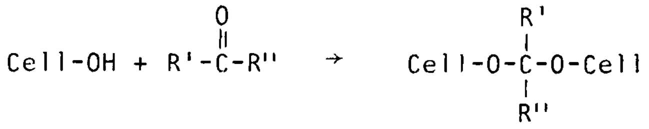
It is also well known that crosslinking reactions in cellulose lead to embrittlement (Gardon and Steele 1961). It is probable that these crosslinking reactions contribute to the increase in specific modulus of paper during natural and accelerated ageing (Graminski 1970) although it has not yet been possible to separate the physical and chemical influences on the elasticity modulus. Back (1967) has suggested that aldehyde groups can react with hydroxyl groups in a crosslinking reaction:



$$R'\text{-}CHO + R''\text{-}OH \rightarrow R''\text{-}O\text{-}\overset{\overset{\displaystyle OH}{|}}{C}\text{-}R' \qquad (1)$$

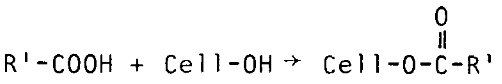
and thereby form hemiacetal bonds. A keto-group on carbon atom 2 or 3 in a cellulose chain would similarly be able to form hemiketal bonds to other cellulose chains. A high content of carbonyl groups (high Cu-number) is therefore favourable for crosslinking reactions.

It is also probable that carbonyl-containing hydrolysis and decomposition products from the cellulose, hemicellulose etc can crosslink the cellulose chains in acetal- and ketal-forming reactions as follows:



$$\text{Cell-OH} + \text{R}'\text{-}\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\text{-R}'' \rightarrow \text{Cell-O-}\overset{\overset{\displaystyle\text{R}'}{|}}{\underset{\underset{\displaystyle\text{R}''}{|}}{\text{C}}}\text{-O-Cell} \qquad (2)$$

It has also been suggested that ethers can be formed (Wilson 1979). Ruffini (1966) suggested that esters could be formed between carboxyl groups (e.g. from uronic acid groups in hemicellulose) and the hydroxyl groups of the cellulose.



$$\text{R}'\text{-COOH} + \text{Cell-OH} \rightarrow \text{Cell-O-}\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\text{-R}' \qquad (3)$$

It is also known that such acid catalysed reactions lead to an excessive hornification (limited swelling during moistening) of the cellulose (Lindström and Carlsson 1982). A higher drying temperature during the drying of paper also leads to a greater hornification of the cellulose (Davidson 1956).

All the reactions above (equations 1-3) are acid catalysed and the wet strength increases with lower pH or in the presence of Lewis acids (e.g. Zn^{2+}), (Wilson 1979, Roberson 1976). Wilson and Parks have also shown that a lower extract pH during natural ageing leads to an increase in the wet strength of the sheet (see fig. 3.6). (Wilson 1980).

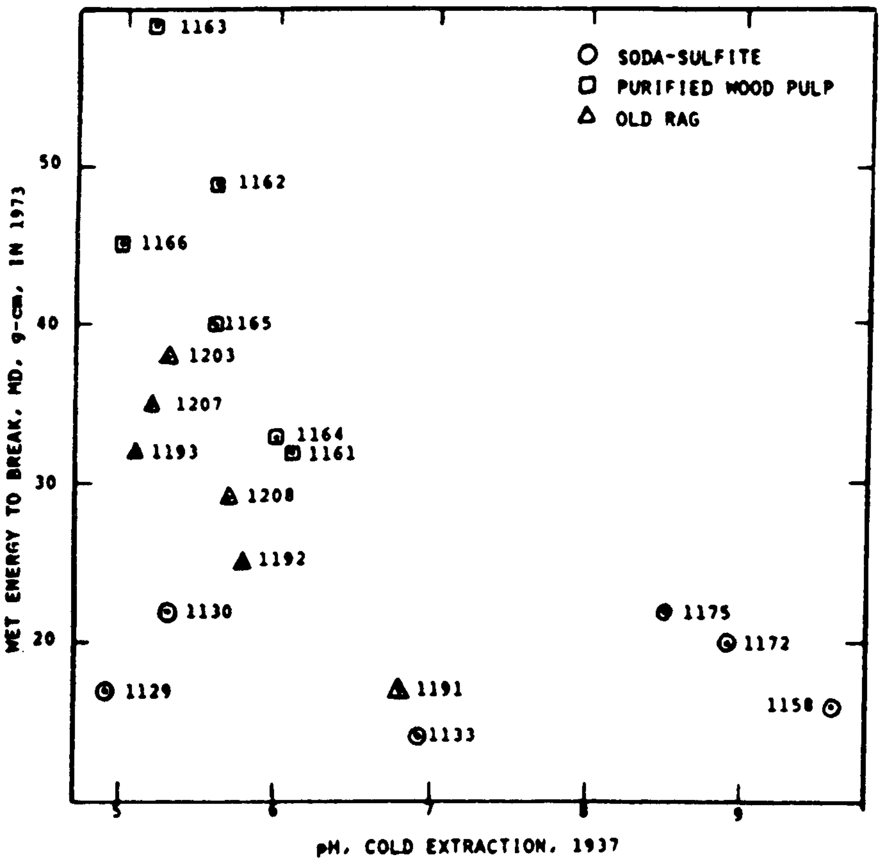


Figure 3.6 Effect of extract pH measured in 1937 on the wet strength measured in 1973 after natural ageing. (Wilson 1980)

3d Changes in the supramolecular structure of the cellulose during ageing

It is well known (Hermans 1949, Howsmon 1949, Bikales 1971) that the crystallinity of the cellulose increases during heterogeneous hydrolysis. The changes occur even at very low degrees of hydrolysis (Sharkov 1960). These phenomena can be attributed to the fact that the cellulose crystal is not perfect and that local conformation variations occur along the cellulose micro-fibril. During hydrolysis, built-in stress concentrations in the crystallite can be released (see section 3a) and the state of order can increase. The relationship is illustrated in fig. 3.7.

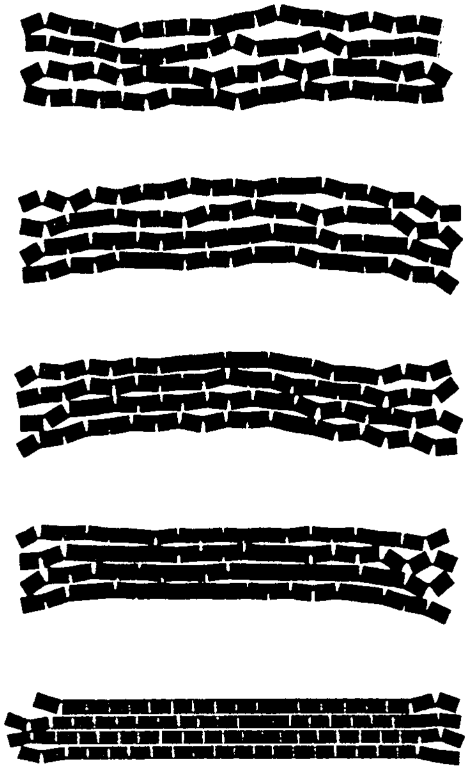


Figure 3.7 Increasing state of order of the cellulose during hydrolytic attack (Atalla 1981).

The phenomenon is well known during the ageing of old cotton textiles etc. The effect is illustrated quantitatively in figure 3.8.

It is probable that the crystallization rate during heterogeneous hydrolysis is dependent on the moisture content/moisture content history of the cellulose etc. It is to be expected that hydrolysis in combination with crystallization gives a more brittle material during ageing.

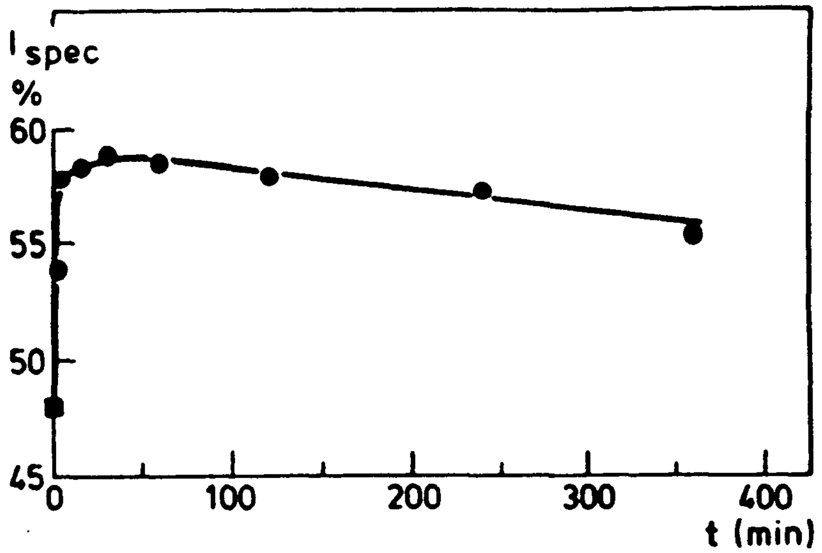


Figure 3.8 The specific crystallinity of dissolving pulp as a function of the hydrolysis time in 2.5 N HCl. (Hattula 1987)

The increase in the elasticity modulus of paper during ageing is probably related to both crystallization processes and crosslinking reactions (Graminski 1970). It is not known whether crystallization can take place in the cellulose without simultaneous hydrolysis.

3e Photochemical ageing reactions

The effect of light on the mechanical properties of paper has not been studied as carefully as the other ageing reactions. It is clear that the mechanical properties deteriorate during light irradiation (Richter 1935). The sensitivity to light of paper increases with increasing lignin content in the pulp and it is therefore relevant to divide the discussion into two sections: the ageing of chemical pulp (with low lignin content) and the ageing of high-yield pulps (with high lignin content).

Chemical pulp

The photodecomposition of cellulose can be divided into two in principle different types of reaction. The first of these is a direct photolysis of cellulose when light of a suitable wavelength is absorbed by the molecule and causes a breakage of chemical bonds. For this to take place, ultraviolet (UV)-radiation with short wavelengths (< 300 nm) is required (Hon 1975). These wavelength ranges do not exist in daylight or in ordinary light sources. This type of ageing is therefore not of interest in connection with normal ageing processes.

Photosensitized decomposition of cellulose is, on the other hand, something which can take place at the lower wavelengths (≈ 300-400 nm) present in normal light sources. The cellulose itself does not absorb this radiation. The radiation must first be absorbed by some other paper component, a so-called sensitizer. These are either impurities or added substances and can after excitation transmit the energy to the cellulose and there initiate decomposition reactions of the same type as those taking place during autoxidation (see section 3b). Few works have investigated which groups of substances or compounds induce these photochemical decompositions. Residual lignin (Hon 1975) and certain metal ions, especially Fe^{3+} (Hon 1975, 1976), have however been shown to have negative effects. Pigments like TiO_2 and ZnO are photochemically reactive and can therefore under UV-radiation give rise to free radicals which decompose the cellulose (see also section 7d). It is also probable that substances which have been liberated during the ageing of the paper and contain UV-absorbing groups can initiate photochemical reactions.

High-yield pulps

The radiation-induced ageing of mechanical pulps is a big problem which can be traced to photochemically induced reactions in the lignin. For a survey article see Gratzl (1985). It is the UV-radiation (290-380 nm) in the daylight which causes these reactions which lead to a rapid reduction in the paper brightness. This reduction is so rapid that paper produced from mechanical pulps and to a certain degree from chemimechanical pulps are only suitable for use for products with a limited functional time, such as e.g. newsprint and magazine paper. At the same time, the reactions lead to a decomposition of the cellulose and increase the content of acid groups in the paper (Lewis 1945).

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4 EFFECTS OF ENVIRONMENT ON AGEING

4a Effects of moisture and temperature

An increase in moisture content leads to a strong acceleration of the ageing of paper (see e.g. Richter and Wells 1956, Luner and Cardwell 1973, Roberson 1976, Arney and Jacobs 1979, Spinner 1962, Wilson and Parks 1979, Graminski and Parks 1979). In general, this applies to properties such as fold number (Luner 1973, Graminski 1979), breaking length (Graminski 1979, Arney 1979) and brightness (Spinner 1962, Arney 1979). The speed increase is however strongly dependent on the type of pulp and on the additives used during the papermaking (Luner 1973).

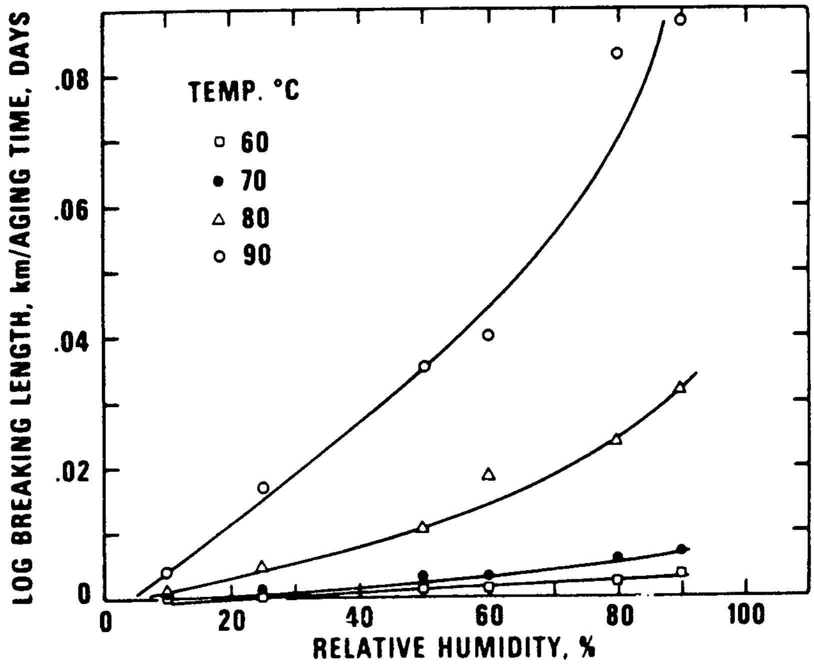


Figure 4.1 *Change in "zero-span" breaking length during the ageing of paper at different temperatures and different atmospheric humidities (Graminski et al 1979).*

As an example, figures 4.1 and 4.2 show the effects of different temperatures and atmospheric humidities on the ageing rate for the so-called "zero-span" breaking length and fold number of paper (Graminski et al 1979).

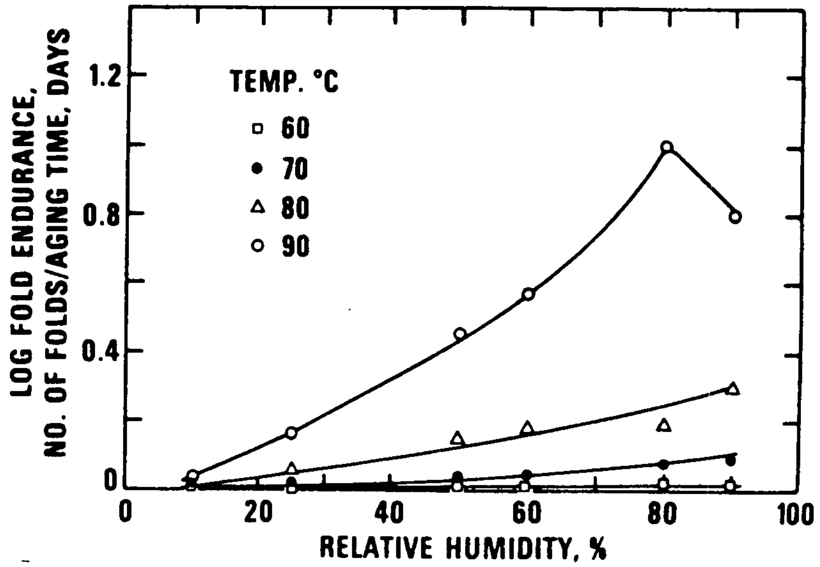


Figure 4.2 Change in fold number during the ageing of paper at different temperatures and different atmospheric humidities (Graminski et al 1979).

Both an increase in atmospheric humidity and an increase in temperature increase the ageing rate. A closer analysis (fig. 4.3) shows that the ageing rate at moisture contents above 2-3% is directly proportional to the moisture content (Graminski et al 1979).

It has been suggested that the first adsorbed water (corresponding to 2-3%) on the cellulose is inactive from a decomposition viewpoint.

In their investigation of the accelerated ageing of paper, Arney and Jacobs (1979) made a distinction between the effects of relative atmospheric humidity on oxidative and on hydrolytic processes.

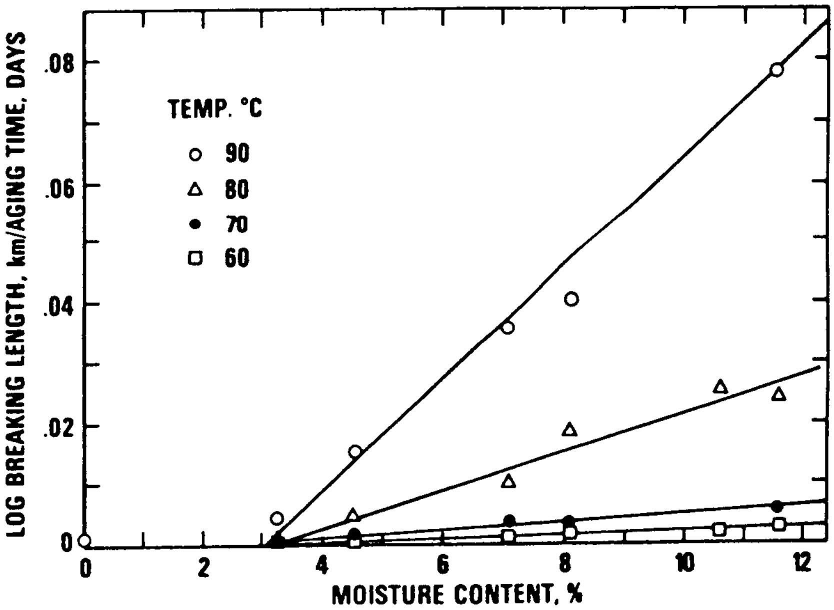


Figure 4.3 Change in "zero-span" breaking length during the ageing of paper at different temperatures and different moisture contents. (Graminski et al 1979).

It was found that an increase in moisture content usually increases the speed of both oxidative and hydrolytic decomposition processes, although in one case (rags) it was noted that the hydrolytically induced yellowing decreased with increasing moisture content.

Croon et al (1965) found however that yellowing because of HCl-release from chlorinated extractive substances decreased with increasing moisture content. This was explained by the fact that the HCl-concentration in the paper became lower the higher the moisture content in the paper. These examples show that the decomposition rate does not a priori have to increase with an increase in moisture content in the paper.

It has also been found that moisture cycling increases the rate of decomposition of paper (Luner 1969, Cardwell 1973). There are probably several reasons for this. Moisture cycling induces stress relaxation in paper and this relaxation involves irreversible property changes in the paper (Wink 1961).

Since paper has built-in stresses and stress concentrations because of the drying process, the separate elements in the sheet structure are exposed to stresses during moisture adsorption. These stresses can lead to failure on the cellulose chains and free radicals can be formed (R·) which then initiate autoxidation in the presence of oxygen ($RO_2\cdot$). The termination of such peroxy radicals gives rise to chemiluminescence, which is a quick, empirically useful method for studying material decomposition (Mendenhall 1977).

Fig. 4.4 shows how chemiluminescence from a paper depends on moisture cycling and how, during moisture adsorption, one obtains a transient signal because of a swelling-initiated rupture of the cellulose chains (Kelly and Williams 1979).

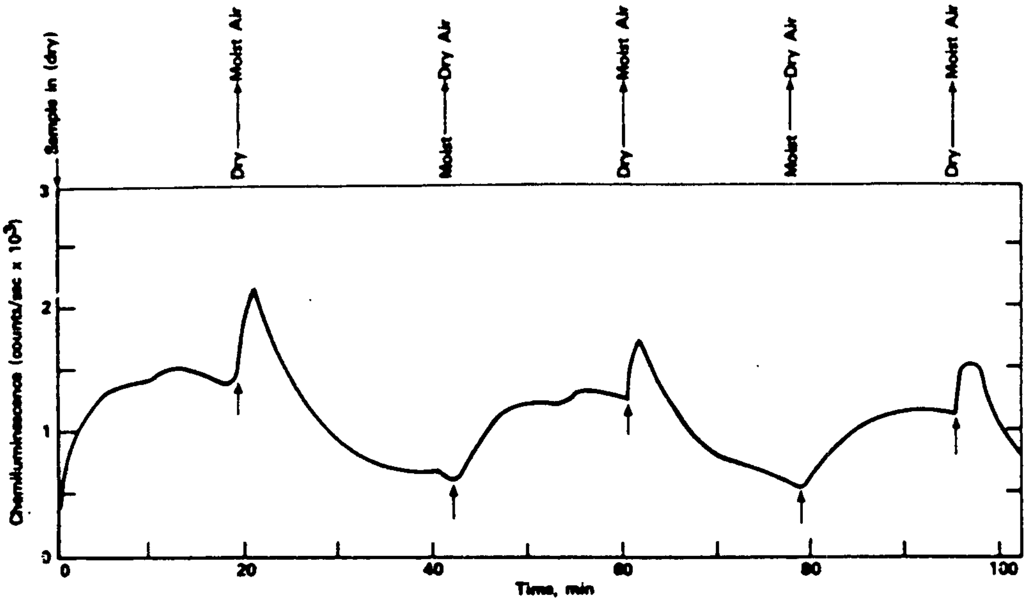


Figure 4.4 Effects of cycling moist and dry air at 70°C on chemiluminescence from paper. (Kelly and Williams 1979).

It is also evident in the figure that the chemiluminescence is higher at a higher moisture content.

Fig. 4.5 shows how the chemiluminescence depends on the temperature and that the calculated activation energy (17-22.6 kcal/mol) is of the same magnitude as that for the accelerated ageing of paper (Gray 1969).

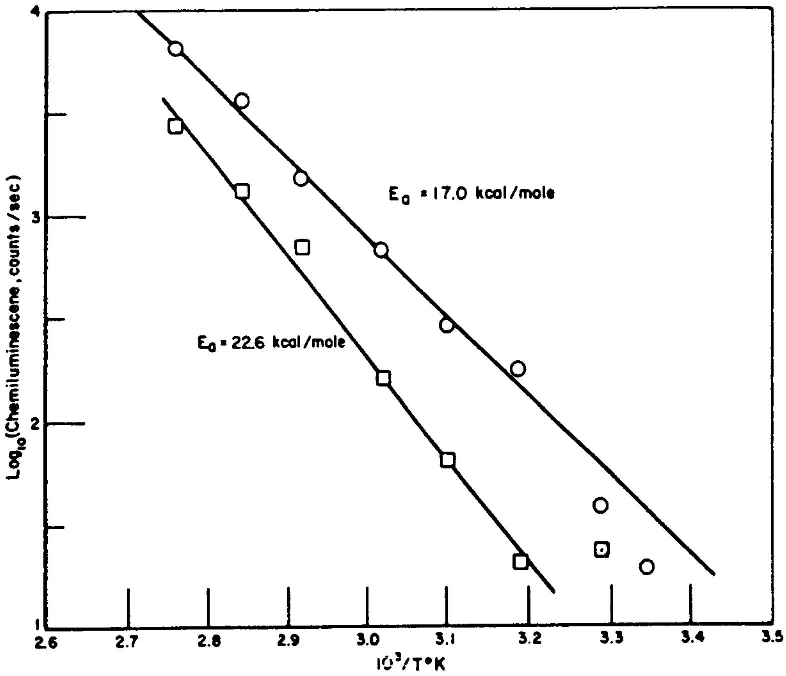


Figure 4.5 Arrhenius plots of chemiluminescence from paper in humid air (□) and paper in dry air (○). (Kelly and Williams 1979)

4b Effect of oxygen

Facts suggest that atmospheric oxidation plays an important role in the ageing of paper. It has been known for a long time that the decomposition rate is significantly lower in the absence of oxygen (Major 1958). (See section 3b).

Arney et al (1979, 1982) investigated the relative importance of atmospheric oxidation during the accelerated ageing of paper made on the one hand from mechanical pulp (newsprint paper) and on the other hand from rags (archive paper).

Figure 4.6 gives examples of such data where the relative ageing rate is given as a function of the relative oxygen content with 1 atm of air as standard state.

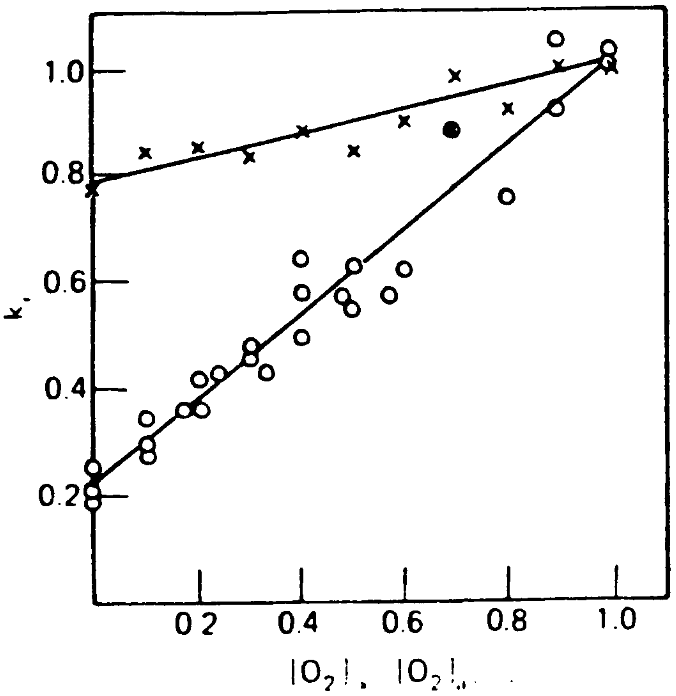


Figure 4.6 *The relative rate of ageing at 90°C versus the relative oxygen concentration. (Arney 1979).*
x = Archive paper/tensile strength at 0% R.H.
o = Newsprint paper/reflectance at 100% R.H.

It is evident that the decomposition rate varies directly with the oxygen content and the change in property dP/dt can therefore be expressed as

$$\frac{dP'}{dt} = k_a \frac{[O_2]'}{[O_2]_{atm}} \cdot f(P) + k_b \cdot f(P) \qquad (1)$$

where P is tensile strength or reflectance, k_a is the rate constant for the oxygen-dependent decomposition and k_b the rate constant for the decomposition which is independent of oxygen concentration.

An illustrative compilation of some data is presented in Table 4.1 where the relative importance of the oxidative processes (% Ox) given by

$$\% \text{ Ox} = 100 \cdot \frac{k_a}{k_a+k_b}$$

has been indicated. In the table, the relative rate of decomposition in dry air compared with that in air at 100% R.H. can also be found.

Table 4.1

The relative importance of oxidative processes and atmospheric humidity during ageing of archive paper and newsprint paper at 90^oC. (Arney 1979).

Archive paper	*RH(%)*	*% Ox*	*Kw*
Reflectance	0	91	1
"	90	45	0.4 ± 0.1
Tensile index	0	43	1
"	90	21	0.08 ± 0.02
Newsprint paper			
Reflectance	0	78	1
"	90	92	0.21 ± 0.02
Tensile index	0	40	1
"	90	80	0.36 ± 0.07

From Table 4.1, the following conclusions can be drawn:

1. The yellowing was caused primarily by atmospheric oxidation both for archive paper and for newsprint.

2. The tensile index loss was caused primarily by oxygen-independent processes except during the ageing of newsprint at 0% R.H.

3. In all cases, both oxidative and non-oxidative processes were of importance for the ageing rate.

In another investigation, which was limited to newsprint, the relative importance of atmospheric oxidation at different ageing temperatures was investigated (Arney 1980). It was found in this particular case that the importance of atmospheric oxidation decreased at lower ageing temperatures.

In chapter 7, the effect of pH on the ageing rate is discussed and it is established that both the oxidative and oxygen-independent ageing processes are composed of acid-dependent and acid-independent components (Arney 1979).

If the rate of ageing is directly proportional to both the oxygen-content and the hydrogen ion concentration, the rate can be described by the expression (Arney 1982):

$$\frac{dP}{dt} = (k_1 \cdot [O_2][H^+] + k_2[O_2] + k_3[H^+] + k_4)f(P) \qquad (2)$$

where k_i are the individual rate constants. The fraction (i) of the total rate of degradation which depends on oxygen-dependent processes can then be expressed as:

$$i = \frac{k_3 \cdot [H^+] + k_4}{k_1[O_2][H^+] + k_2[O_2] + k_3[H^+] + k_4} \qquad (3)$$

The value of i can then be determined directly as the ratio of the rate of ageing in a N_2-atmosphere to the rate of ageing in air.

Experimental results relating to i = f(pH) are shown in figure 4.7 for archive paper. The accelerated ageing was performed at $95^{\circ}C/100\%$ R.H. in closed containers.

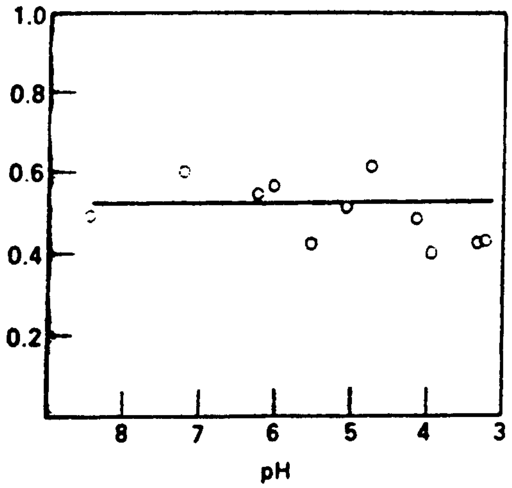


Figure 4.7 *The ratio of the rate of ageing of archive paper in N_2-atmosphere to the rate in air (i-value) at different pH values. Tensile index. (Arney 1982)*

It becomes clear that i with respect to tensile index is independent of pH for both archive paper and newsprint. This means that k_2 and k_4 in equation (3) can probably be neglected.

In a similar way, Arney and Novak (1982) investigated i = f(pH) for the diffuse reflectivity (500 nm) (fig. 4.8). For both newsprint and archive paper, the oxidative processes dominate the yellowing processes in the pH-range mentioned (pH>4), and it is only for archive paper at very low pH-values that the oxygen-independent processes dominate.

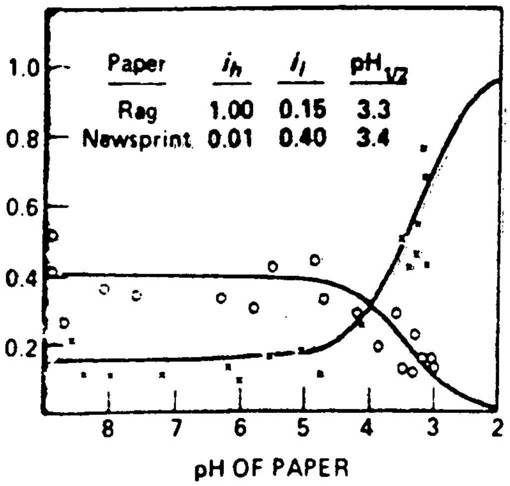


Figure 4.8 *The ratio of the rate of ageing of archive paper (x) and newsprint (o) in* N_2*-atmosphere to the rate in air (i-value) at different pH values. The reflectivity at 500 nm. (Arney 1982)*

4c Air pollution

The effects of air pollution on the ageing stability has, with the exception of studies of the effects of SO_2, only been investigated to a very small extent. Besides particulate pollution (carbon, fly ash, salt particles, soot, spores etc), it is the contents of SO_2, NO_x and O_3 which expose paper to hydrolytic or oxidative attack (Wilson and Parks 1979, Wessel 1970).

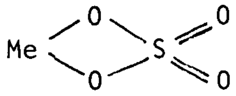
Jarrel et al (1936, 1938), and Langwell (1956) found at an early stage that the sulphuric acid content was higher at the edges of books than in the middle of the pages. The accumulation of sulphuric acid in books during storage could initially amount to 0.2%/year before decreasing later on. The sulphuric acid content seldom amounted to more than 0.8% at the edges of books (Langwell 1956). Hudson (1967) also

also showed that in a comparison between books from the 17th and 18th centuries which had been stored in different places, books where the amount of air pollution was higher had a lower pH-value. It is probable that the effects of air pollution on the acidity of paper are greater than is usually considered to be the case (Wessel 1970).

In extreme cases, it has been shown that the fold number can decrease by 15% within 10 days at a SO_2-content of 0.5 ppm, a value which is not unusual in strongly polluted areas (Wessel 1970). The contents of SO_2, NO_x and O_3 vary strongly in different areas and contents up to a couple ppm are not abnormal maximum values, even though the mean values lie in the range 0.03-0.2 ppm for SO_2 and NO_x and 0.05-0.65 ppm for O_3 in USA 1964 (Wilson 1979). In photochemical smog, much higher values of primarily ozone, peroxy-acyl nitrates (PAN) and NO_x can occur (Wessel 1970).

The effects of SO_2-sorption in paper have been studied primarily by Langwell (1952, 1953, 1955, 1956 and 1959) and Hudson et al (1956, 1961, 1964, 1967 and 1968). Langwell noted early that the occurrence of metal ions such as Fe, Cu, Mn strongly accelerated the absorption of sulphur dioxide in paper. The effect of the transition metals is probably that they accelerate the catalytic oxidation of SO_2 to SO_4^{2-} (Schenk 1987) according to the equation:

$Me\ (SO_2)_{ads} + O_2 \rightarrow$



(1)

It has also been shown that chelate-forming inhibitors such as EDTA strongly reduce the absorption of sulphur dioxide in paper (Langwell 1953, 1955, Hudson 1961). Figure 4.9 shows how the sulphur absorption varies with contact time for some different types of pulp in contact with 0.5% SO_2 (Hudson 1961).

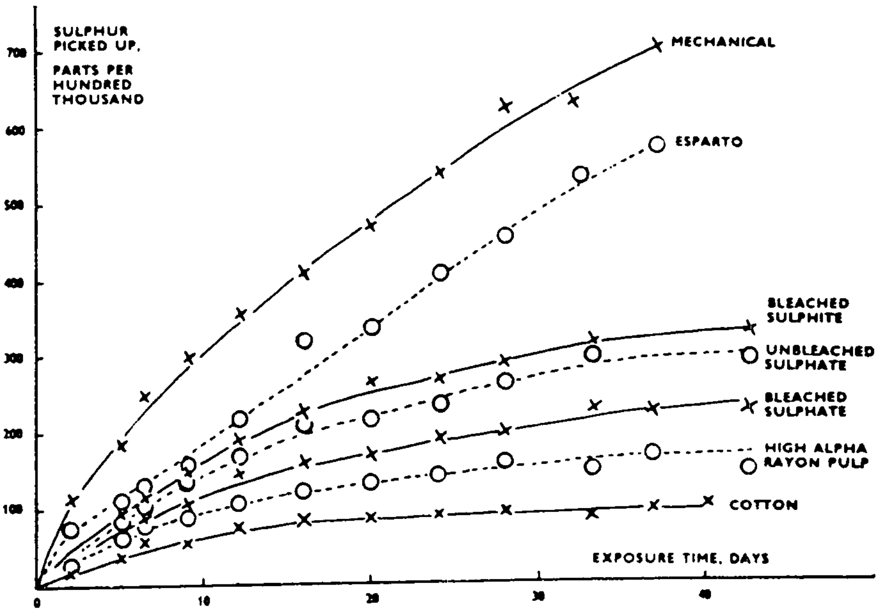


Figure 4.9 Sulphur absorption (^{35}S) in some different types of pulp in contact with 0.5% SO_2. (Hudson 1961).

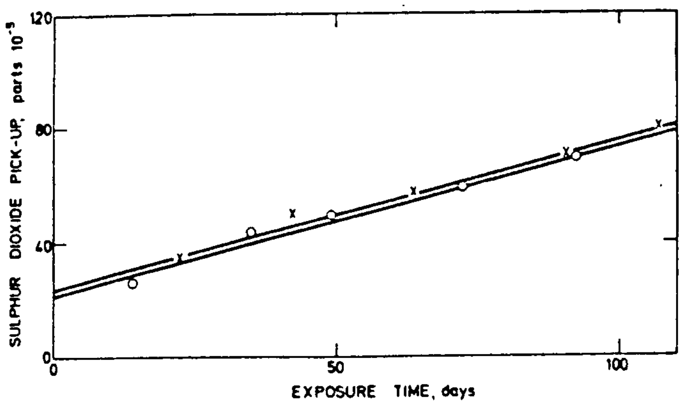


Figure 4.10 Effect of relative humidity on sulphur absorption (^{35}S) at 25°C and 10 ppm SO_2. (Edwards and Hudson 1968).

In general, it is true that pulp types with a low content of lignin or hemicellulose have a lower absorption of ^{35}S. The sulphur absorption is not linearly related to the SO_2-content in the gas state; it has been noted that the sorption is proportional to the square root of the partial pressure of the gas. (Edwards and Hudson 1968).

The relative humidity affects the initial SO_2-absorption (< 48 hours). Initially, an increase in relative humidity increases the sulphur dioxide absorption strongly, but after 48 hours the SO_2-sorption is independent of the moisture content (Edwards and Hudson 1968).

It is probable that this is related to an increased initial formation of sulphurous acid in the paper (because of higher moisture content in the sheet).

An increase in temperature leads to an increased absorption of $^{35}SO_2$. In the temperature interval 10-30°C, the calculated activation energy lay between 6 and 8 kcal/mol (Edwards and Hudson 1968).

It is also known from autoradiographic studies of $^{35}SO_2$-absorption that hand sweat increases the $^{35}SO_2$-absorption. This has even lead to a method for the detection of fingerprints on paper (Grant and Hudson 1963).

4d Effect of perspiration on the ageing permanence of paper

It is a well known phenomenon (Sundberg 1986) that during the circulation of e.g. bank-notes, the acidity in the paper increases. This depends on the fact that one of the main components in sweat is lactic acid. In practice, the effect becomes accelerated, since lactic acid destroys the hydrophobicity of so-called resin-sized paper. A reduction in the hydrophobicity of the paper means that the absorption of liquid (and thereby sweat) increases, which worsenes the surface strength on contact with water/moisture. During resin sizing, the resin acids are coordinated to aluminium atoms which leads to strong hydrophobic particles/surface films. The lactic acid catalyses the degradation of the metal soaps through competition with the carboxyl groups of the resin acids and consequent protonization of the soaps.

The increase in acidity of the paper catalyses, in the usual way, hydrolytic and oxidative degradation processes in the paper.

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5 PHYSICAL AGEING

The physical ageing of a material can be said to be a sort of consolidation process where the molecules with time adjust their positions so that a closer structure is formed. The ageing process is thus characterized by a decrease in volume with time. This volume reduction in turn leads to changes in the physical properties of the material. An increasing degree of brittleness is for example often observed in a material which has been stored for a long period of time.

The phenomenon of physical ageing has been studied in detail in the case of amorphous synthetic polymers. The standard work in the field is called "Physical Aging in Amorphous Polymers and Other Materials" written by L.C.E. Struik (1978) and a Swedish survey has also been published (Klason et al. 1983). Although the interest in physical ageing has so far mainly been associated with amorphous thermoplasts, the phenomenon appears in all types of materials, e.g. natural polymers, semi-crystalline thermoplasts, thermosets, rubber, inorganic glasses, metals and margarine.

The purpose of this chapter is to describe briefly the phenomenon of physical ageing and how this process affects the mechanical properties of the material. Part of the increasing degree of brittleness of paper with time can probably be credited to physical ageing, although this mechanism naturally does not alone cause the deterioration in paper properties during storage for a long period of time.

5a Brief physical background

The situation for amorphous plastics is here first described, and only later is the physical ageing of semi-crystalline polymers discussed. If the temperature is higher than the glass transition temperature (T_g) of the polymer, the molecular mobility is high and the system is in thermodynamic equilibrium. If the polymer is cooled relatively quickly to a temperature $T < T_g$, the low mobility of the molecules at this temperature will, somewhat simplified, prevent them from assuming their lowest energy state. The available volume will not be used in an optimum way. The plastic will be in a non-equilibrium state and have a volume which is slightly larger than that which corresponds to the equilibrium state. The system strives, however, to attain equilibrium and this leads to a reduction in volume with time. Since the molecular mobility is so low, this is a process which can take a very long time. It is this process which is usually called <u>physical ageing</u>. The changes in structural density with time are reflected in changes in other properties of the polymer, e.g. its stiffness.

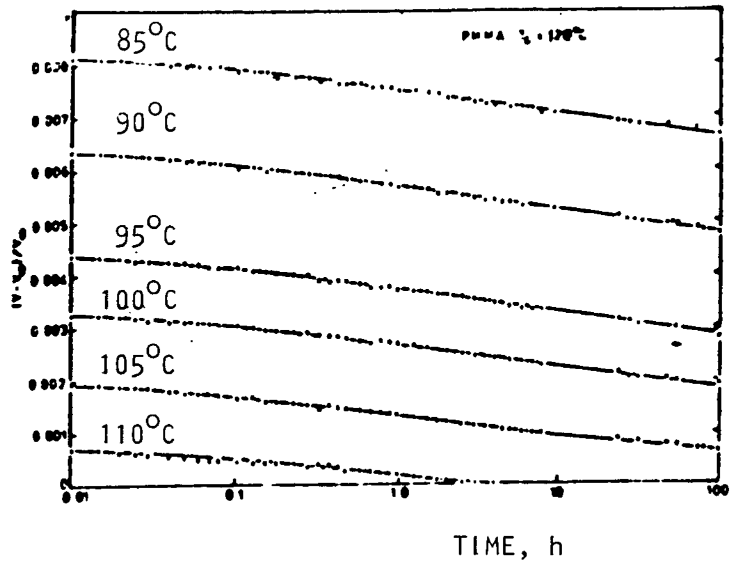

Figure 5.1 The change in volume as a function of time for PMMA which has been cooled from 120°C to a number of different temperature levels.

The fact that the volume changes gradually with time after a change in temperature is shown in Figure 5.1. Polymethylmethacrylate (PMMA) in equilibrium at 120°C (> T_g) has been cooled to different temperatures and the volume has thereafter been measured as function of time at the lower temperature (Hutchinson, Bucknall, 1980).

As can be seen, the change in volume continues over a long period of time and the changes are fairly small. It should be mentioned here that one usually discusses physical ageing in terms of the free volume. The free volume is the volume space between the molecules, i.e. the difference between the volume of the test sample and the total intrinsic volume of the molecules. It is the free volume which determines the mobility of the molecules and which decreases during the ageing process.

From what has been said above, it follows that the physical ageing is reversible. If the temperature is increased to a level higher than T_g, all effects of ageing are eliminated (high molecular mobility). If the temperature is again lowered below T_g, the ageing process starts from the beginning. The fact that the physical ageing is reversible, distinguishes it from chemical ageing which is associated with a chemical change in the molecular structure. Chemical ageing causes an irreversible change in the polymer.

5b Influence of physical ageing on creep processes

During the ageing process, the volume available for molecular movement (the free volume) decreases successively and the time scale for these movements becomes displaced towards longer times. Mechanical flow processes, the rate of which is also determined by the molecular mobility, will be affected to a corresponding degree. Flow of polymer materials is usually described in terms of a spectrum of relaxation or retardation times if the deformation is not too great. During ageing, all relaxation times are displaced along the time axis in the same way, which means that the shape of the flow curve does not change during physical ageing but that the position of the curve along the time axis is affected. In order to investigate the effect of the ageing process on the mechanical properties of polymers, the flow behaviour is therefore often measured after different ageing times. In most cases, creep experiments seem to be used here, but stress relaxation can also be used.

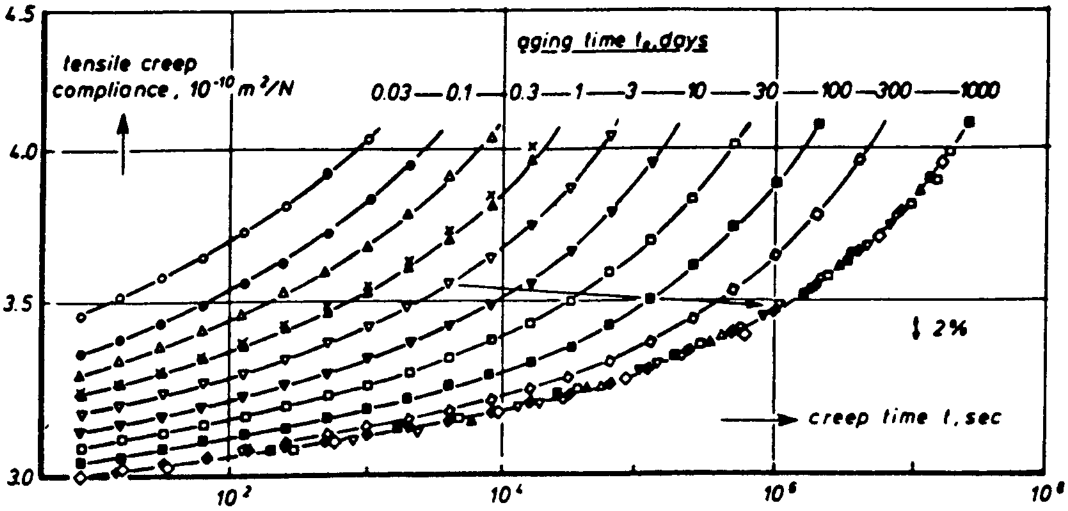

Figure 5.2 Creep curves for PVC at 20^{o}C after different ageing times (t_e) at this temperature. The samples have been rapidly cooled from 90^{o}C (Struik, 1978).

Figure 5.2 shows creep curves for polyvinyl chloride (PVC) at 20^{o}C (Struik, 1978). During creep, the sample is exposed to a constant stress σ_0 and the resulting strain $\varepsilon(t)$ is measured as a function of the time t. In Figure 5.2, the deformation is expressed as creep compliance

$$J(t) = \varepsilon(t)/\sigma_0 \qquad (1)$$

The PVC-samples have here been cooled from equilibrium at $90^{\circ}C$ ($>T_g$) to $20^{\circ}C$ and the creep behaviour has been measured after different ageing times (t_e) at this temperature.

In this type of measurement, the deformations are so small that the material can be considered to be linearly viscoelastic. The creep time is always much shorter than the ageing time in order to avoid effects of physical ageing during the measurement (Struik, 1978). Figure 5.2 shows that the curves are displaced towards longer times with increasing ageing time. The material becomes stiffer the longer the ageing process has proceeded.

If the curves are displaced horizontally (and with a slight vertical shift), a master curve can be constructed, see Figure 5.2. The shape of the curve is thus not affected by the ageing time. Struik (1978) also found the behaviour shown in Figure 5.2 in other amorphous plastics and in such materials as asphalt, natural resins, pressed cheese powder, supercooled molten sugar and epoxy plastic (a crosslinked polymer). Since a master curve can be constructed by displacing the creep curves more or less horizontally along the time axis (the small vertical shift being neglected) the creep compliance corresponding to the ageing time t_e can be converted to the corresponding creep compliance at the ageing time t'_e according to

$$J_{t'_e}(t) = J_{t_e}(at) \qquad (2)$$

where a is the displacement factor. Log a indicates how far the creep curve at t_e must be displaced along the time axis to coincide with the creep curve at ageing time t'_e. Figure 5.3 shows how log a varies with ageing time (log t_e) for PVC. Results for samples which have aged up to 1000 days (approximately 3 years) are included in this figure.

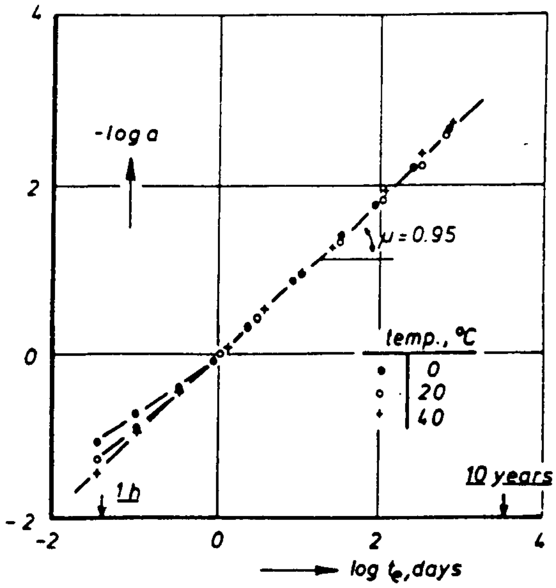

Figure 5.3 *The displacement factor (- log a) as a function of the ageing time (log t_e) for PVC which has been cooled from 90°C(>T_g) to 0, 20 and 40°C. Log a is the displacement relative to the creep curve measured for an ageing time of 1 day.*

The influence of the physical ageing on the creep process can thus be characterized by the derivative

$$\mu = - d \log a / d \log t_e \qquad (3)$$

It is here assumed that log a is positive if the horizontal displacement takes place from right to left. In this case, μ is equal to unity, see Figure 5.3, and is independent of the ageing time. It is also evident that the displacement rate μ is practically independent of the temperature in the interval 0-40°C. For many other amorphous systems, $\mu \simeq 1$ over a fairly broad temperature interval (Struik, 1978). Close to T_g, μ decreases rapidly to become zero when $T > T_g$. At temperatures $> T_g$, the material does not age. Even though $\mu \simeq 1$ over a fairly broad temperature interval, the rate of displacement will decrease slightly at low temperatures, see Figure 5.4. In the temperature interval where $\mu > 0.65$, ageing is said to be completely developed. The lower temperature limit for this range is considered by Struik (1978) to be given by the temperature for the secondary transition which has the highest temperature.

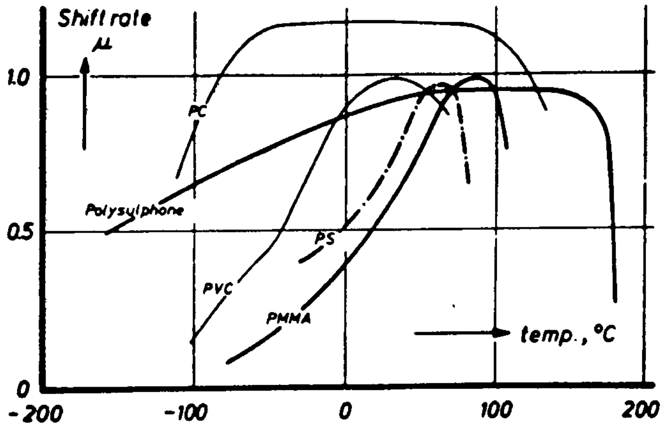

Figure 5.4 The rate of displacement μ *as a function of the temperature for PMMA, PVC, polycarbonate (PC), polysulphone and polystyrene (PS) (Struik, 1978).*

The lower temperature limit for the ageing range is thus "unique" for each amorphous substance, while the upper is given by T_g.

It is not especially surprising that $\mu \simeq 1$ for most amorphous systems. Struik (1978) has shown that the molecular mobility (M) in a material which is far from its equilibrium state decreases with the ageing time t_e according to:

$$M \sim k/t_e \qquad (4)$$

where k is a constant. Since the mechanical relaxation times are inversely proportional to M, the following is directly obtained:

$$\mu = \frac{d \log a}{d \log t_e} = - \frac{d \log M}{d \log t_e} \simeq 1 \qquad (5)$$

The physical ageing can in principle proceed for a very long period of time, as is evident in Figure 5.5. This shows the time which is required to attain thermodynamic equilibrium in a material at different degrees of supercooling $(T-T_g)$. The curve is based on certain assumptions, but it should still be clear that at a supercooling of -40°C, it takes many years before equilibrium is attained.

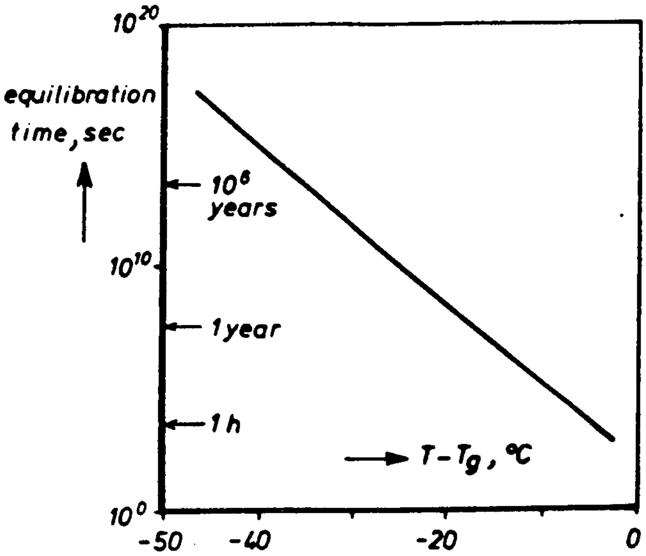

Figure 5.5 *The time t_∞ required to attain thermodynamic equilibrium as a function of $T-T_g$ $(T<T_g)$ (Struik, 1978).*

Experimental results concerning physical ageing over very long periods of time are not reported to any great extent, depending partly on the fact that it is primarily during the last decade that the phenomenon has been studied systematically.

It should be stressed here that the rate of displacement μ is in fact a tool for predicting how the physical ageing affects the flow behaviour of a material.

5c Effects of physical ageing on other mechanical properties

Besides the influence of the flow behaviour of amorphous polymers described above, the physical ageing will also affect the other mechanical properties. Among the most important effects of an increased ageing time, the following can be mentioned:

- The yield point increases
- The impact value decreases if the material is fairly tough (the material becomes more brittle)
- The stretch to failure can decrease

5d Physical ageing of semi-crystalline polymers

What has been said so far concerns primarily the physical ageing of amorphous synthetic polymers. Results for semi-crystalline polymers have so far not been available to the same extent, but a series of newly published works by Struik (1982, 1986a,b) shows that effects of ageing can be very pronounced for this group of materials also.

If the amorphous phase in the semi-crystalline polymer has a T_g-value which lies above the storage temperature, these polymers age in the same way as amorphous polymers. Interesting in this context is that Struik (1976, 1982) noted that semi-crystalline polymers also age above the T_g for the amorphous phase. This has been observed for polyethene, polypropene and polyamide 6.

The ageing effects at $T > T_g$ are assumed to depend on the fact that the amorphous phase is disturbed close to the crystallites. In this region, the molecules have a lower mobility than in a completely amorphous material, see Figure 5.6.

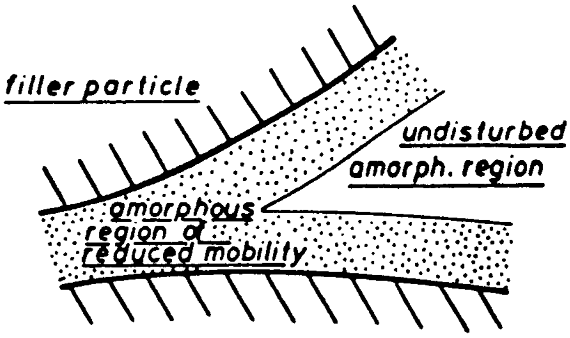

Figure 5.6 The structure of the amorphous phase close to a crystallite surface (or a filler surface) (Struik, 1978).

As a consequence of the reduced molecular mobility, the semi-crystalline polymers will show a relatively broad T_g-range compared with a completely amorphous material, the parts of the amorphous phase which lie closest to the crystallite surface showing the highest glass transition temperature. This explains why semi-crystalline polymers age at $T > T_g$. At a given temperature $> T_g$, a part of the amorphous phase will still be a glass and will age in the same way as has been described earlier.

It should be pointed out that this picture is slightly speculative. Several of the ageing phenomena which are noted can also be explained if the semi-crystalline polymers undergo secondary crystallization after the rapid cooling.

5e Physical ageing of natural polymers

The phenomenon of physical ageing is something that is expected to occur in all materials in some temperature interval.

Natural semi-crystalline polymers are no exception here. It has e.g. been observed that wool ages with a μ-factor of about 1 (Chapman, 1975a,b). It was also noted that if wool was exposed to water, this had the same effect as heating to a temperature > T_g, i.e. the ageing effects were erased.

No investigations concerning the effect of physical ageing on the mechanical properties of paper seem so far to have been performed. In one work, however, the physical ageing of textile fibres, including cotton and rayon fibres has been studied (Breese et al. 1986). Figure 5.7 shows how the creep curves are shifted to the right with increasing ageing time, which is typical of a physical ageing process, for cotton fibres. Effects of earlier ageing were erased for these samples by exposing them to a combination of moisture (reduction of T_g) and increased temperature.

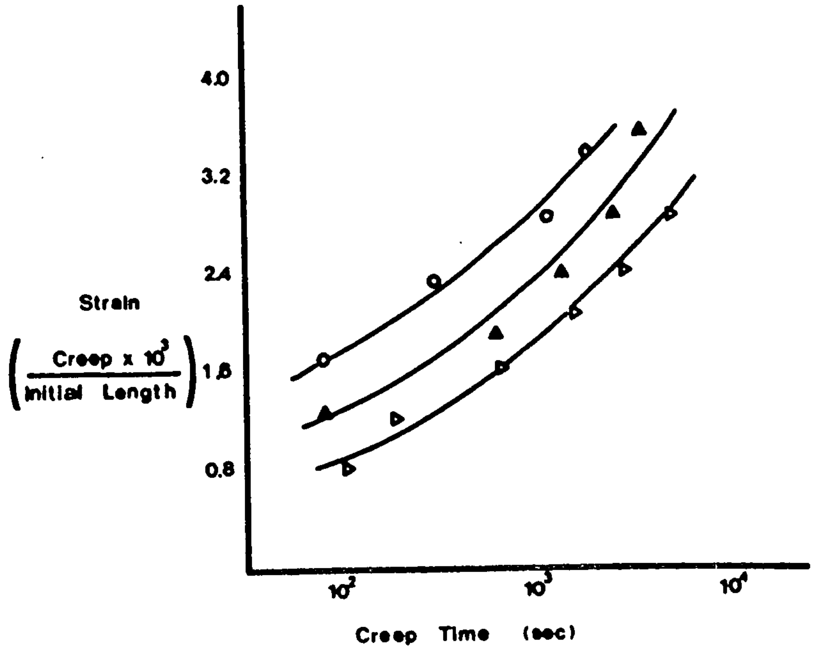

Figure 5.7 Creep curves for cotton fibres which have aged at room temperature for (○) 28, (▲) 49 and (▷) 105 hours (Breese et al. 1986).

A 400 year old cotton fibre was used in a creep experiment. Thereafter the fibre was exposed to a temporary moisture and temperature treatment and the creep behaviour was again measured. The creep curve for the treated fibre was displaced considerably towards shorter times, which shows that physical ageing is of importance also in the case of very old fibres.

Figure 5.8 shows the displacement factor (log a) as a function of the ageing time (log t_e) for cotton fibres.

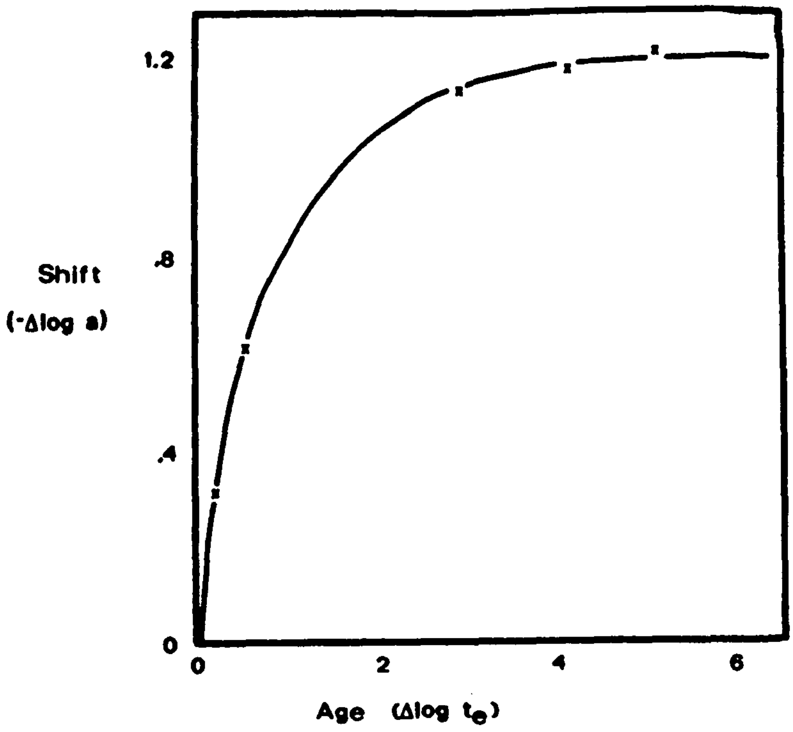

Figure 5.8 The displacement factor log a vs. log t_e for cotton fibres at room temperature.

Since log a gradually assumes a constant value independent of the ageing time, this means that the displacement rate μ approaches zero after long periods of time. This can mean that thermodynamic equilibrium has been attained, but it is possible that the complicated morphology of the material affects the time dependence of μ, (cf. Hedvat, 1981; Cowie and Mc Ewen, 1979). More investigations are required within this section to clarify the ageing kinetics.

For shorter ageing times, μ was about unity for cotton fibres at 25 and 50°C, whereas the rate of displacement was 0.82 at 75°C. For rayon, a reduction in μ was also observed with increasing temperature, from 0.87 at 25°C to 0.58 at 75°C.

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6 MICROBIAL DECOMPOSITION OF PAPER

This section is devoted solely to microbial damage to books and archive paper in libraries and is not concerned with possible measures, chemical treatments etc, which can prevent microbial attack.

Most studies deal with the isolation and identification of micro-organisms from damaged paper. No descriptions of the extent of the damage have however been found. In the case of damage to individual objects, it can, however, be seen on published pictures that the damage can be very extensive. Many studies of the cellulose activity of isolated micro-organisms have also been carried out.

The damage is mainly of three different types: 1) direct decomposition of the paper, 2) different forms of discoloration and 3) sticking together of sheets of paper. The latter can occur when the paper has become completely soaked by water, during e.g. floods (Strzelczyk and Leznicka 1981). Rich growth of micro-organisms followed by the production of slime causes the pages of paper to stick together. This must, however, be regarded as an exceptional form of damage.

6a Micro-organisms which occur

Bacteria

Most of the investigations only concern fungal flora. Information about the occurrence of bacteria is therefore scarce. Lazar and Dumitru (1972) detected the occurrence of cellulolytic bacteria of the families Cytophaga, Cellulomonas and Cellvibrio. Bacillus and Pseudomonas species also occurred. Strzelczyk and Leznicka (1981) found bacteria from the following families: Bacillus, Pseudomonas, Escherichia, Streptococcus and Micrococcus. Cellulolytic bacteria, Sporocytophaga and Cytophaga also occurred.

Czerwinska et al (1953) isolated 13 species of actinomycetes from old documents and manuscripts.

Fungus

Basidiomycetes

Only four different species of basidial fungus have been isolated from paper, Pellicularia isabellina (Kowalik et al 1962), Coprinus sp. (Kowalik et al 1962), Sistotrema brinkmannii (Savulescu and Lazar 1971) and Polyporus tulipiferae (Savulescu and Lazar 1971). The house fungus, Serpula lacrymans, during attack on wood in buildings where books or archives are stored, could also cause great damage to the paper. Such damage has not however been reported.

Ascomycetes and Fungi imperfecti

Fungi from these groups dominate completely in the myco-flora. Especially common are different species of Aspergillus and Penicillum. Species from among others the following families were also commonly occurring: Chaetomium (several species), Cladosporium, Fusarium, Stachybotrys, Stemphylium and Trichoderma. The myco-flora can be said to be relatively unspecific and is similar to that which arises during mould attack on wood under unfavourable conditions.

A study of the occurrence of air-borne spores in a library in India has been carried out by Vittal and Glory (1985).

6b Damage

a) Decomposition of the paper

It is completely clear that strong microbial decomposition can take place. Closer studies of decomposed paper do not however seem to have been carried out.

b) Discoloration

Different types of discoloration seem to be the most frequent type of damage. Discoloration can depend on the fact that the micro-organisms during growth on paper form pigment, but it can also be related to the fungus mycelium in the cases where the hyphae are dark coloured.

A common type of discoloration is called "foxing", which means that brown to yellow-brown (rust-coloured) spots are formed in the paper (Baynes-Cope 1976, Nol et al 1983, Press 1976). The spots are caused by fungus with colourless hyphae. A hypothesis has been presented, which says that the fungi produce phenols which cause discoloration (Nol et al 1983). The influence of ferric salts has been discussed (Nol et al 1983, Press 1976). The presence of ferric salts does not seem necessary for the appearance of "foxing", but for some species of fungus the discoloration becomes stronger in the presence of iron. Species from the Aspergillus, Penicillum and Gliocladium families have been isolated from "foxing"-spots (Nol et al 1983).

6c Cellulolytic activity of the micro-organisms

Fungi and bacteria which grow on paper do not necessarily have any cellulolytic ability since paper contains substances other than cellulose. Such substances, i.e. starch and adhesive substances and perhaps even dirt, can also constitute a nutritional substrate and thereby permit the growth of different non-cellulolytic micro-organisms.

The mechanisms for decomposition of cellulose are not dealt with in this study. For more detailed information, Eriksson (1981) is referred to. It is, however, completely clear that a very large number of the micro-organisms isolated have the ability to decompose cellulose. Bacteria from the Cytophaga, Cellulomonas, Cellvibrio and Sporocytophaga families are cellulolytic. (It is known that several of these bacteria form strongly coloured pigments during the decomposition of cellulose. It is not, however, known whether this takes place in the type of paper with which this investigation is concerned.) Actinomycetes isolated from paper also produced cellulase. Many species of Aspergillus, Penicillum and Chaetomium have a very good cellulose-degrading ability.

6d The living conditions of the micro-organisms

a) pH

Kowalik et al (1962) indicate that only cellulolytic fungus occur at pH 4, since the bacteria have a pH-interval of 6.8-8.0. Actinomycetes grow best at pH 5.0-8.0. These authors also indicate that a paper which has a pH of 4.0-6.0 decomposes quicker than a paper with a pH of 7.0. The pH of the paper can also affect the colour and intensity of possible discolorations.

b) Temperature

Information about the temperature requirements of the micro-organisms is sparse. Kowalik et al (1962) say that growth occurred at temperatures up to about 44°C. Optimum conditions for growth were reported within an interval from 22 to 32°C. No studies of the effect of low temperatures seem to have been performed. Other studies of mould show, however, that a large number of the reported fungi can also grow at temperatures slightly above the freezing point, some even at a few degrees below zero.

c) Humidity conditions

Typical for several mould fungi is that they can grow in spite of a low moisture content both in the substrate and in the surrounding air. Ohtsuki (1985) has reported that Aspergillus vitricolae can grow on fibres at 60% RH. At 100%, on the other hand, it did not grow at all. Another Aspergillus-species growed best at 70-90% RH. Considerably less growth occurred at 60 and 100% RH. Aspergillus fumigatus and A. terreus have shown growth on paper at 32.5% RH. The latter fungus caused "foxing" even at this low moisture content.

Summarizing articles about microbial decomposition of paper have been written by, among others, Greathouse and Wessel (1954) and Turner (1967). These authors also discuss different possibilities of protecting paper from microbial attacks.

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7 EFFECT OF FIBRE RAW MATERIALS, THE PAPERMAKING PROCESS AND PRINTING

7a Fibre raw materials - cooking/bleaching

Fibre raw materials

It is well established that in order to make a paper with maximum ageing stability one should choose a fibre raw material with the highest possible content of α-cellulose (Wilson, 1979, 1980; Stamm, 1959) and with as low content of carbonyl groups (Cu-number) as possible.

Pure raw materials such as cotton therefore have a potential superiority over bleached kraft or sulphite cellulose and these in turn are clearly superior to so-called mechanical or chemimechanical pulps from an ageing point of view. In this section, only cooking and bleaching processes for so-called chemical bleached pulps are discussed. Besides cellulose, these contain hemicellulose, extractive substances and lignin residues which affect the ageing stability of the material considerably.

Since the ageing is essentially a hydrolytic/oxidative process, the fact that the hemicellulose has a considerably higher rate of hydrolysis is important (Springer, 1962). The ageing process (autohydrolysis) is also catalysed by acetic acid which is produced during the cleavage of acetyl groups of the hemicellulose (present in sulphite pulp). The hemicellulose also has a higher accessibility than the cellulose since it is amorphous with the exception of the hemicellulose which has crystallized on the cellulose surfaces during the cooking process (Yllner and Engström, 1956). It is therefore clear that a high hemicellulose content gives a paper with poor ageing stability. It is e.g. well known that so-called "dissolving pulps" (alkali-extracted sulphite pulp, prehydrolysed kraft pulp etc.) with a low hemicellulose content give paper with a better ageing stability than conventional bleached pulps (Wilson and Hebert, 1969; Roberson, 1976).

It is not possible to give a clear answer to the question of whether kraft or sulphite pulp gives paper with the best ageing stability or whether softwood or hardwood is the best fibre material. The softwood contains more lignin and O-acetyl groups and has a higher content of glucomannan but has on the other hand a lower content of glucoronoxylan than hardwood. The kraft process results in a higher glucoronoxylan content but in a lower glucomannan content than the sulphite process (Rydholm, 1965).

Table 7.1 shows some analyses of the chemical composition of softwood and hardwood pulps from the sulphite (acid) and kraft processes.

Table 7.1

Chemical composition of some dried bleached pulps (Lüner 1969)

	Chemical composition, % of o.d. pulp		
Type	*Cellulose*	*Glucomannan*	*Glucoronoxylan*
	Sulphite process		
Spruce-strong	85	10	5
Spruce-soft	89	7	4
Birch-soft	89	3	8
Beech-soft	88	3	9
	Kraft process		
Scotch pine	81	8	11
Birch	73	0	27
Beech	76	0	24

The higher content of hemicellulose containing uronic acid in the kraft pulp should lead to a poorer ageing stability of this pulp. In addition, the sulphite pulp is more easily bleached than kraft pulp, which in general leads to less oxidative attack during the bleaching process.

An essential difference between sulphite pulp and kraft pulp which should be of great importance is that kraft pulps in general give papers which are less brittle than papers based on sulphite pulps. This is reflected in the fact that the fold number, tear index etc. are higher for kraft pulps. Page (1983) has speculated that this may depend on the fact that the supramolecular structure of cellulose microfibrils changes during the alkaline cook.

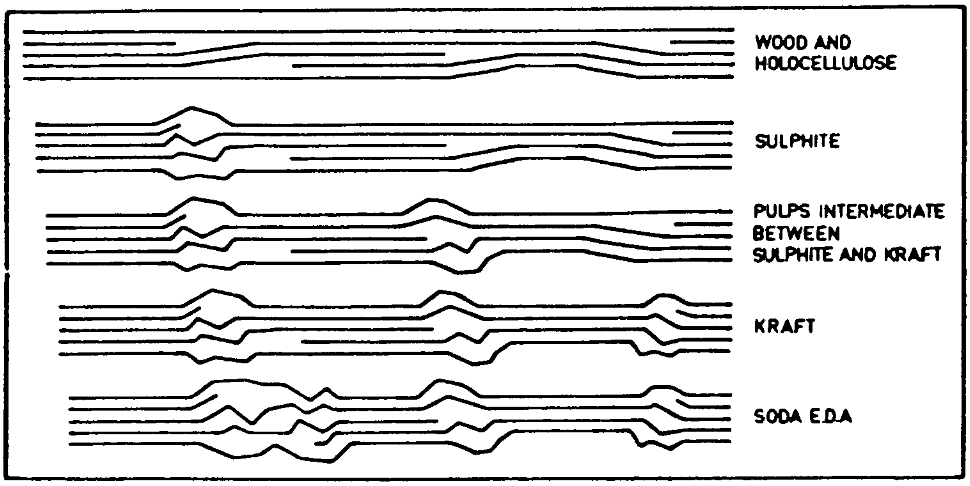

Figure 7.1 Transformation of paracrystalline to amorphous regions in cellulose microfibrils (Page 1983)

Fig. 7.1 shows how it is imagined that the supramolecular structure of the microfibril changes during an alkaline treatment. The paracrystalline parts of the cellulose are transformed to amorphous regions during an alkaline cook. The phenomenon can be looked upon as a partial mercerisation of the cellulose and the model is based on the fact that the crystallite length of the cellulose measured as LODP ("Levelling Off Degree of Polymerisation") for the cellulose decreases during an alkaline treatment. It can be imagined that the treatment introduces more amorphous material into the fibre and makes the crystallite tougher. Brecht (1940) showed for example at an early stage that alkaline treatment of a sulphite pulp gave a pulp with higher fold number.

Brightness stability - Hemicellulose

The importance of hemicellulose and oxidized groups on the light stability of pulps during accelerated thermal ageing has been investigated carefully and these results constitute an important frame of reference for the further discussion. It should, however, be noted that such thorough studies of the mechanical properties of paper have not been carried out and no quantitative comparison should therefore be made (Luner, 1973; Roberson, 1976). Decomposition products of the fibre which cause brightness instability should, however, also contribute to a large extent to the mechanical ageing instability of the paper. The contribution of the hemicellulose to the brightness instability of pulps includes conversion to furfural or 5-hydroxymethyl-furfural, which form coloured condensation products in a complex pattern. Pentoses, hexoses and hexuronic acids are also converted to phenols, acetophenones, chromones and enones such as reductinic acid, which are all very reactive intermediaries in the production of strongly coloured substances. These transformations include enolising, dehydration, fragmentation and condensation reactions (see e.g. Theander, 1987). The reactions are accelerated by high temperature and low pH.

Brightness stability of oxidized cellulose

It was discovered early that the yellowing of pulps was accentuated by strongly oxidative bleaching agents (Spinner, 1962). The oxidative attack then accelerates the hydrolysis of either the cellulose or the hemicellulose.

The yellowing is measured as so-called post-coloration number (PC-number) and is defined as:

PS = 100{(k/s) after ageing - (k/s) before ageing}

where k is the light absorption coefficient and s the light scattering coefficient of the paper. The yellowing depends on the presence of many types of oxidized groups. Ketonic and aldehydic groups (but not hemiacetals) increase the yellowing, which is shown by the fact that the yellowing is related approximately linearly to the copper number (Fig. 7.2).

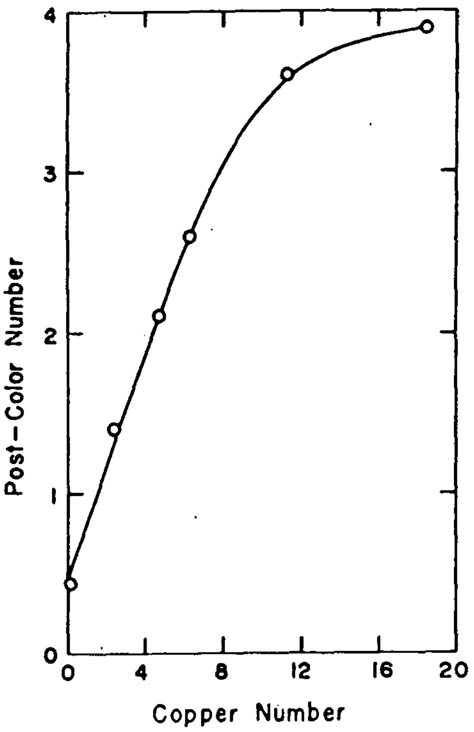

Figure 7.2 PC-number versus Cu-number for periodate oxidized cotton linter (Spinner 1962).

Reduction of the ketonic and aldehydic groups with $NaBH_4$ reduces the yellowing tendency strongly, as is illustrated in figure 7.3.

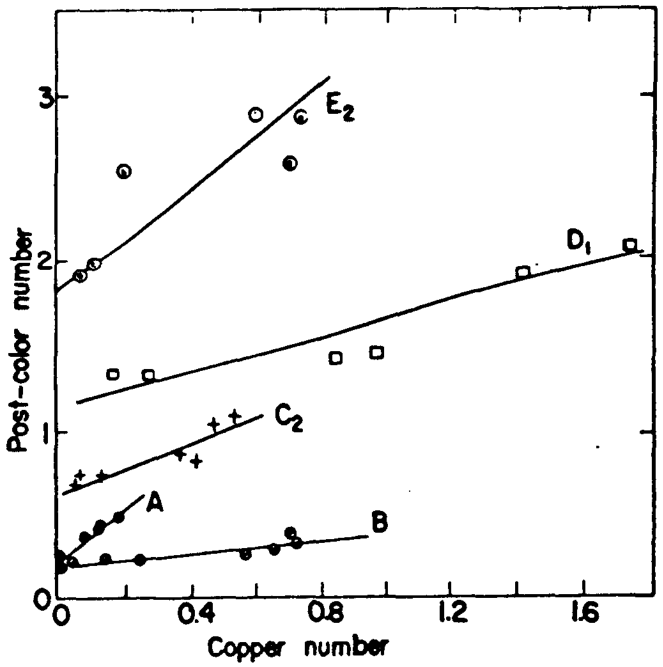

Figure 7.3 PC-number versus Cu-number for $NaBH_4$-reduced pulps (Spinner 1962).

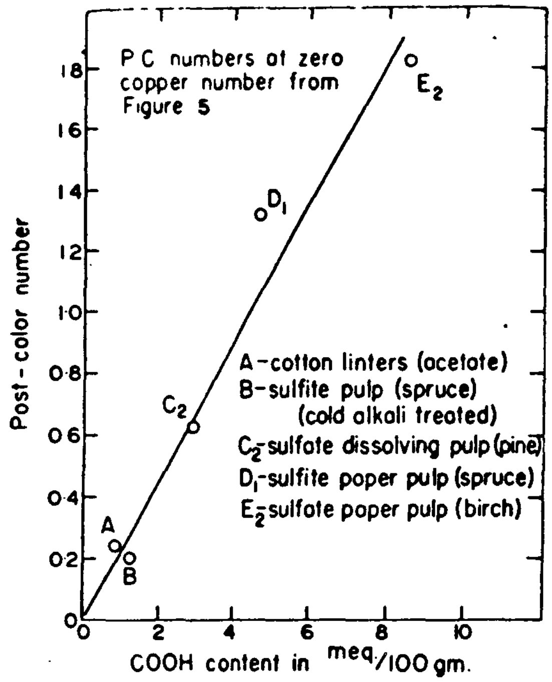

Figure 7.4 PC-number versus carboxyl group content after $NaBH_4$-reduction of different pulps (Spinner 1962).

It was also noted that after reduction the yellowing (in fig. 7.3) was directly proportional to the COOH-content in the pulp (see fig. 7.4).

The dependence of the yellowing on the oxidation of cellulose can be summarized in the following way (Croon et al, 1965):

1. *The PC-number is proportional to the Cu-number except when different types of pulp are compared.*

2. *The effect in 1 depends primarily on the carbonyl groups introduced.*

3. *Carboxyl groups lead to a smaller yellowing tendency than ketonic or aldehydic groups.*

4. *The yellowing tendency is, however, proportional to the uronic acid content in the pulp.*

Bleaching

Since carbonyl groups make the cellulose alkali unstable (β-elimination), an alkaline treatment of the pulp always leads to the disappearance of the most oxidized pulp and this increases the ageing stability of the pulp. In general, it is true to say that chlorine and hypochlorite bleaching produce a pulp with a higher yellowing tendency (higher carbonyl content) than chlorine-dioxide-bleached or chlorite-bleached pulps (Wilson and Parks, 1983; Croon et al, 1965). By oxidation of ketonic and aldehydic groups in a final stage, the brightness stability can increase according to 3 above. Reducing end groups do not contribute to the yellowing tendency (Wilson and Parks, 1983).

Chlorinated lignin and chlorinated extractive matter

Another important cause of yellowing is chlorinated lignin (Howard and Histed, 1964) and chlorinated extractive matter (Croon and Olsson, 1964). Howard showed that the yellowing tendency of a large number of sulphite and kraft pulps (bleached in different ways) was directly correlated to lignin-bound chlorine (see fig. 7.5).

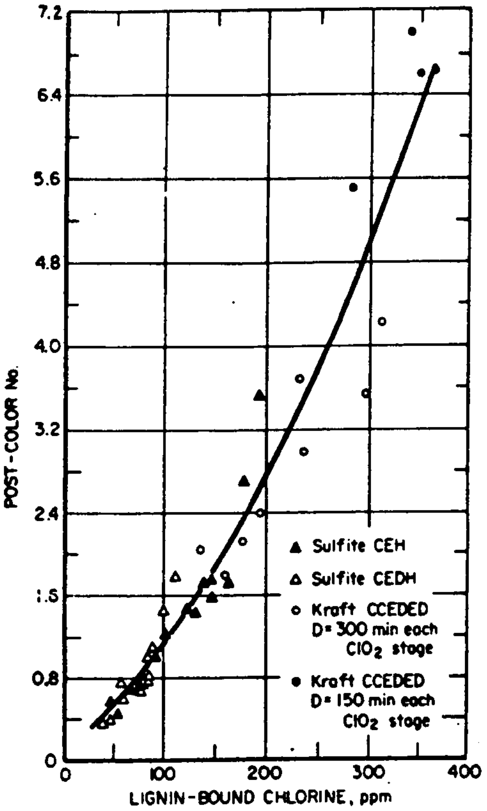

Figure 7.5 PC-number versus content of lignin-bound chlorine in the pulp. (Howard and Histed 1964).

Extractive matter is also chlorinated during chlorine bleaching and this chlorinated extractive matter becomes dark coloured when heated, as opposed to non-chlorinated extractive matter.

Fig. 7.6 shows how HCl is released from an ethanol-benzene extract of bleached birch kraft pulp.

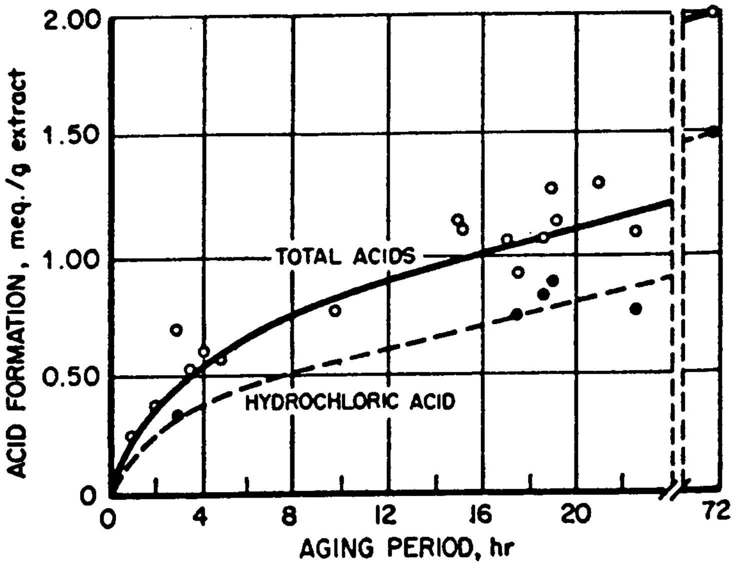

Figure 7.6 Acid produced during heating of an ethanol-benzene extract from bleached birch kraft pulp. (Luner 1969).

This depends on the fact that chlorinated hydrocarbons eliminate HCl and that conjugated systems of double bonds are formed. The dark coloration of the pulp also depends, however, on acid hydrolysis processes because of HCl-elimination.

7b pH/buffer capacity

It is a well established fact that the pH of the paper (measured as so called extract-pH) is of great importance for the deterioration in the mechanical properties of the sheet during accelerated ageing (Wilson and Parks, 1980, 1983; Barrow, 1963).

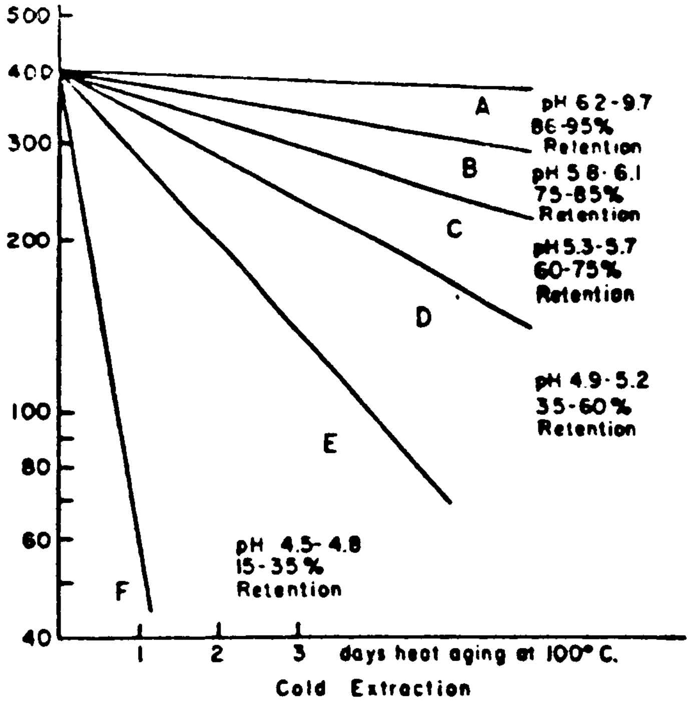

Figure 7.7 Retention of the fold number after accelerated ageing plotted against the extract-pH of the sheet (Barrow 1963).

Fig. 7.7 shows an example taken from Barrow where the fold number retention after accelerated ageing was plotted against the extract-pH of the sheet.

How the fold number retention after natural ageing depends on extract-pH is not as well documented. Fig. 7.8 gives, however, an example of such a relationship.

Arney and Chapdelaine (1979) investigated how both mechanical and optical properties were affected by pH during accelerated ageing (90°C/100% R.H.). These authors used the so called time/ratio-technique in order to obtain quantitative values of the relative rate of ageing.

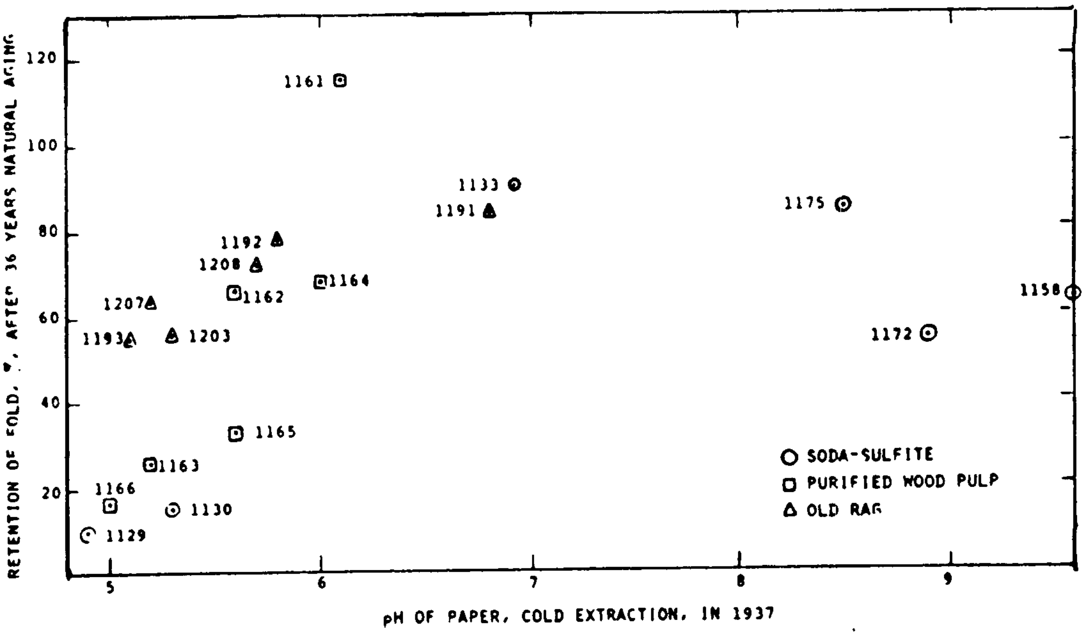

Figure 7.8 Retention of the fold number after natural ageing plotted against the extract-pH of the sheet. (Wilson 1980)

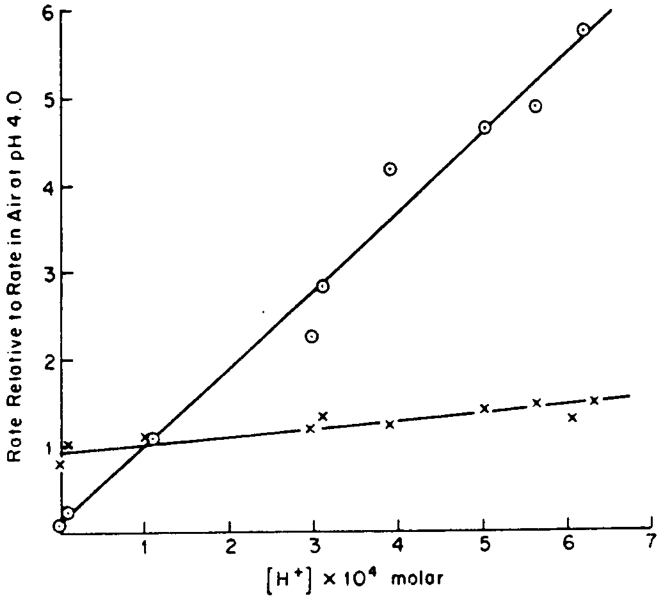

Figure 7.9 Relative rate of ageing with regard to changes in tensile index (⊙) and brightness (x) at different extract-pH levels in archive paper (90°C/ 100% R.H.) (Arney 1979).

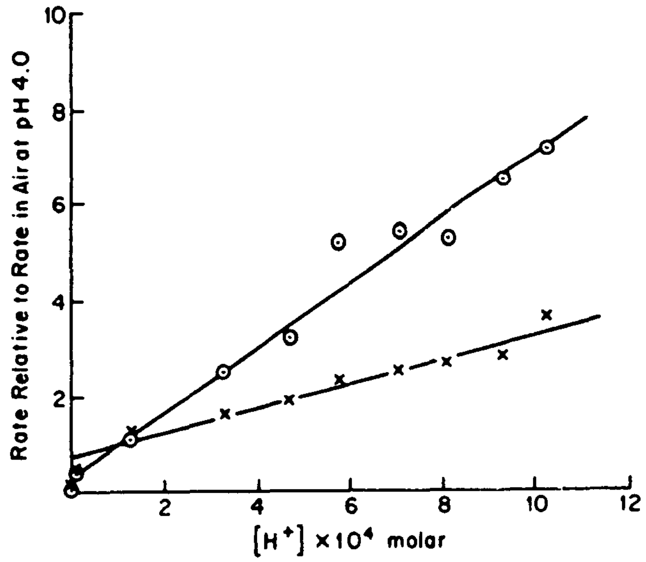

Figure 7.10 Relative rate of ageing with regard to changes in tensile index (⊙) and brightness (x) at different extract-pH levels in newsprint (90°C/ 100% R.H.) (Arney 1979).

Figs. 7.9 and 7.10 show the effect of hydrogen ion concentration (expressed as extract pH) on the relative rate of ageing (compared with the rate of ageing at pH 4.0) with regard to brightness and tensile index for archive paper (rag-based fibre) and newsprint (mechanical pulp).

These data show that the rate of ageing is directly proportional to the hydrogen ion concentration. The yellowing, however, is not as dependent on the hydrogen ion concentration and takes place even under neutral conditions. It should be noted that the acidity of commercial papers (extract pH > 4) is in general lower than the pH-range here investigated.

If the ageing takes place in a nitrogen atmosphere instead, the rates of ageing are similarly proportional to the hydrogen ion concentration but the rate of ageing is considerably lower. The rates of ageing in air and N_2 can therefore be expressed as:

$$\text{air:} \quad k_{air} = k_{\alpha 1} [H^+] + k_{\alpha 2} \qquad (1)$$

$$N_2\text{:} \quad k_{N_2} = k_{\beta 1} [H^+] + k_{\beta 2} \qquad (2)$$

Table 7.2

Experimental values for the rate constants in equations (1) and (2) determined relative to the rate at pH 4 in air (90°C/ 100% R.H.) (Arney 1979)

Property	$k_{\alpha 1}$	$k_{\alpha 2}$	$k_{\beta 1}$	$k_{\beta 2}$
	Newsprint			
Tensile index	0.68±0.09	(0.32±0.60)	0.36±0.05	0.17±0.28
Reflectance (500nm)	0.26±0.05	0.74±0.29	0.03±0.25	0.21±0.16
	Archive paper			
Tensile index	0.89±0.11	(0.11±0.42)	0.38±0.05	(0.0±0.2)
Reflectance (500nm)	0.09±0.05	0.91±0.21	0.11±0.02	0.21±0.10

The experimental results for the mechanical and optical properties are summarized in table 7.2. These data give an overall picture of the importance of pH in the presence and absence of oxygen. It is, however, not known whether these effects during accelerated ageing agree with the effects during natural ageing. In summary, it is important to note that both the hydrolytic and the oxidative processes are pH-dependent and it is to be expected that similar relationships apply during natural ageing.

Since the acidity of paper increases during storage depending on oxidative processes as well as absorption of SO_2 from the air (Hudson, 1967), it is important that the paper also has a certain buffer capacity in order to resist ageing. This buffer capacity is most easily introduced into the paper in the form of carbonates (Ba, Ca, Mg).

It is also known that the counter-ion to the carboxyl group plays an important role both for the brightness stability and the mechanical ageing stability of the sheet. Koura and Krause (1978) thus found for example that the Ca^{2+}-form was more stable than the Na^{+}-form. The theoretical basis is, however, weak in this latter field.

7c Effect of metal ions

Metallic contamination can occur in paper in a number of different forms such as counter-ions to ionized groups (e.g. carboxyl/sulphonic acid groups), as salt, metal hydroxide, oxide or in a pure metallic state. Reactions and/or equilibrium constants are similarly indeterminate in the complex matrix which the cellulose fibre constitutes. The effects of metal ions on the ageing stability of paper are therefore best discussed in terms of some fundamental reaction mechanisms which seem to be of importance in the context. The effects of metal ions such as iron and manganese on the oxidation of adsorbed SO_2 and SO_3 in paper were discussed earlier in chapter 4c.

Many metal ions of interest can be hydrolysed (e.g. Al, Fe) and displace hydrogen ions during reaction with water according to the following basic pattern: (Baes and Mesmer, 1976; Rubin, 1974).

$$M^{z+} + zH_2O \rightarrow M(OH)_z + zH^+ \qquad (3)$$

These hydrogen ions can of course then induce e.g. hydrolysis and crosslinking reactions in secondary reactions. The metal hydroxides can then polymerize and finally be transformed to oxides with further hydrogen ion formation. Metal hydroxides/oxides therefore catalyse cellulose hydrolysis even in the absence of oxygen (Czepiel, 1960). The reactions are usually irreversible and are favoured by high temperature.

Different metal ions can function as catalysts for

a) cellulose hydrolysis (Czepiel, T.P. 1960)
b) oxidation reactions including photooxidation (Williams, J.C. et al 1977; Hon, N.S. 1975, 1981; Shanan, C.J. 1986)

Metal hydroxides/oxides themselves cause a decrease in brightness during ageing when the hydroxides are transformed to oxides (Czepiel, T.P. 1960). These dark coloured compounds can also induce photooxidation by functioning as photosensitizers (Hon, D.N. 1981).

The decomposition of cellulose is more accentuated the more easily hydrolysed the metal salt is, i.e. in the order $Fe^{+++} > Fe^{++} > Cu^{++} > Mn^{++}$. Manganese was even found to have a certain protective effect. A large part of the effect can probably be attributed to the effect of the hydrolysis on the acidity of the paper.

Autoxidation of cellulose is a free radical mechanism (see section 3b) and the transition metals catalyse the cleavage of the cellulose peroxide molecules according to the following pattern (Shahan and Hengemihle, 1986):

$$\text{Cell-OOH} + M^{z+} \rightarrow \text{Cell-OO}\cdot + H^+ + M^{(z-1)+} \qquad (4)$$

$$\text{Cell-OOH} + M^{(z-1)+} \rightarrow \text{Cell-O}\cdot + OH^- + M^{z+} \qquad (5)$$

This catalysis mechanism is that which is most common in the transition metal catalysed autoxidation of organic substrates, although other possibilities exist (Hipp and Busch, 1978). Catalytic effects of metal ions on the oxidation of cellulose under alkaline conditions have been studied extensively in cooking and bleaching contexts but the effects of metals on autoxidation in paper (in ageing contexts) have not been the subject of intense study (Williams et al, 1977; Hon, 1981; Shahan, 1986). Much work has been carried out on the importance of metal ions for the brightness stability of pulps (Czepiel, 1960; Spinner, 1962 and 1966; Hon, 1981; Kleinert and Marracini, 1962, 1963, 1966; Hart, 1981). The transition metals Fe, Cu and Mn all catalyse autoxidation.

It has been shown that neutralization with bicarbonate reduces the catalytic effect of Fe on the fold number of papers during accentuated ageing but that bicarbonate has no effect on Cu (Shahani, 1986). It has not been proven whether this effect is an inhibition of the autoxidation or a reduced hydrolytic decomposition. It is known that the ligand to the metal ion is of importance and that it is possible to change the catalytic activity of the metal ion strongly through complex formation. (Shahani, 1986).

It is well known that autoxidation of cellulose decreases in the presence of magnesium compounds even though the mechanism is not known. It has been suggested that magnesium can form complexes with free radicals (peroxides) and inhibit these and in this way reduce the decomposition. (Croon and Andrewa, 1971; Samuelson, 1970).

It has also been suggested that magnesium salts can form complexes with transition metals like Cu and Fe. (Robert and Viallet, 1971; Gilbert et al, 1973; Samuelson and Stolpe,, 1974; Isbell et al, 1975; Ericsson et al, 1971).

There is, however, no evidence of the formation of such complexes during the acidification of paper with e.g. $Mg(HCO_3)_2$. Treatment with $Mg(HCO_3)_2$, however, inhibits the

Cu-catalysed oxidative decomposition of paper (Williams et al, 1977) and these inhibition mechanisms are probably of great interest in paper conservation contexts.

7d Effects of additives during papermaking

The additives used in papermaking can be roughly divided up as follows:

a) Filler/pigment
b) Hydrophobic agent
c) Wet and dry strength agents including surface sizing chemicals
d) Tinting colours and optical brightening agents
e) Coating chemicals
f) Process chemicals (retention agents, dewatering agents, defoamers, biocides etc.)
g) Substances for pH-adjustment including alum

For natural reasons, only a few of the range of additive chemicals used in papermaking have been evaluated with regard to their importance for the ageing stability of paper. The literature is often contradictory (Luner, 1969) and it should be easier to make a general estimate of their effect on the ageing stability from a theoretical viewpoint.

With regard to fillers and pigments, it was observed early that $CaCO_3$ was favourable for the ageing stability (Jarrel and Veitch, 1936). The fillers can otherwise be regarded as inert and only secondary factors such as adsorbed metal ions, contamination and so on need to be considered. With regard to pigments like TiO_2 and ZnO, their photoreactivity must be taken into consideration since these pigments absorb UV-radiation and produce free radicals which initiate the decomposition of cellulose (Zeronian, 1977; Kleinert, 1971; Wilson, 1955; Egerton and Shah, 1968).

The hydrophobic agents can be divided into natural and synthetic types. The natural (resin acids) are always used together with the addition of aluminium sulphate, and it is difficult to distinguish between the effects of the resin acid and those of the aluminium sulphate. The resin acids autoxidize quickly and the acid decomposition products are of course not favourable for the ageing stability (Hon, 1981). The synthetic alkyl-ketene-dimer-based hydrophobic agents which are used in the manufacture of archive pergament paper can in general be considered more stable than resin-based hydrophobic agents. Fat chains, waxes and so on can of course be attacked oxidatively in a normal way (Hon, 1981).

In the case of dry strength agents, modified starches are used as additive in stock and surface applications. Bearing in mind the fact that surface sizing starches are decomposed enzymatically or thermochemically and are also easily hydrolysed, these must be considered to play a negative role in the paper similar to that of the hemicellulose in the fibre. Similar arguments apply to stock starches which are, however, used in smaller amounts and are not decomposed like surface-sizing starches. In surface sizing contexts, gelatin and polyvinyl alcohol are also used. Gelatin can be expected to have a certain buffering effect in the sheet. Synthetic dry strength agents occur relatively seldom and the additives are sparse, which is why they, like the process chemical additives (group f), are probably relatively uninteresting from an ageing stability point of view.

In general, wet strength agents cause crosslinking reactions which should not be favourable for the toughness of the paper. The addition of a wet strength agent, however, often increases the initial fold number of the paper (Williams, 1981).

It has been speculated that the addition of tinting colours is negative for the brightness stability of paper (Hon, 1981). Optical brightening agents are used to a large extent in papermaking and since their fluorescence depends on the absorption of UV-radiation, they should in principle be able both to protect the cellulose and to accelerate the decomposition through photosensitizing. In a specific investigation (Dahl, 1965), however, no effects of optical brightening agents (stilbene derivatives) were found on the stability of paper during accelerated ageing or during exposure to UV-radiation. In general, it should be observed that the optical brightening agents in themselves often have very poor light stability.

Systematic investigations of the effects of coating on ageing stability are, in general, missing (see discussion Luner and Cardwell 1973). The coating colour consists of a pigment (e.g. kaolin, $CaCO_3$, TiO_2) with dispersing agent (polyacrylic acid), binder (e.g. styrene-butadiene, PVAc-latex or starch) and water retention agent (e.g. CMC). It can be noted that coating colours are alkaline and often contain $CaCO_3$ even when they are used in the coating of acid hydrophobated papers. This fact should be positive for the ageing stability of the paper.

7e Effect of sheet structure

The tensile failure of paper is initiated mainly by two processes. The failure can take place either through the breaking of individual fibres (cohesive failure type) or through the breaking of fibre-fibre bonds (adhesive failure type). Which failure mechanism predominates depends on factors such as type of fibre (length), fibre treatment (beating) etc. The failure mechanism is also dependent on the type of load to which the paper is exposed. (Cf. section 2 "Fold number and folding endurance")

Cohesive failure can be expected to predominate in sheet structures with weak fibres but strong fibre-fibre bonds (well beaten pulps). Adhesive failure predominates in structures which are weakly bonded but with strong fibres. Adhesive and cohesive failure normally appear simultaneously, however, in ordinary writing and printing papers. The relative importance of cohesive and adhesive failure can be easily varied, e.g. by varying the clamping length in the tensile testing of paper. With a short clamping length (shorter than the mean fibre length) the tensile strength is dominated by the strength of the fibres in the paper, whereas with a longer clamping length failure can be cause both by fibre failure and fibre bond failure.

Fig. 7.11 shows the effect of accelerated ageing on the strength of paper tested at two different clamping lengths. (Britt and Yiannos, 1964).

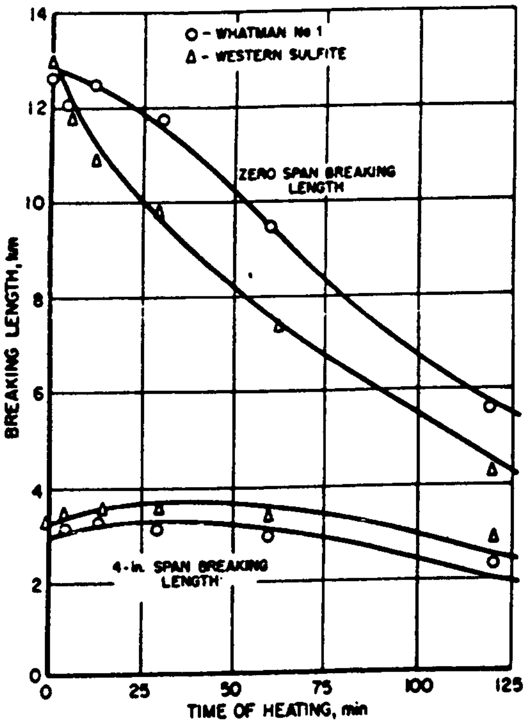

Figure 7.11 *Effect of heating on the "zero span" tensile strength with 4 inches clamping length (Britt and Yiannos 1964).*

The figure shows that the tensile strength decreases strongly during thermal ageing if it is measured with a short clamping length whereas only a small effect of thermal ageing is found when the tensile strength is determined by the normal procedure. These results show that it is the fibre strength which decreases during thermal ageing and not the fibre-fibre bond strength. In a more quantitative analysis of this phenomenon, Page (1969) has shown that the bond strength actually increases during thermal ageing. (See fig. 7.12).

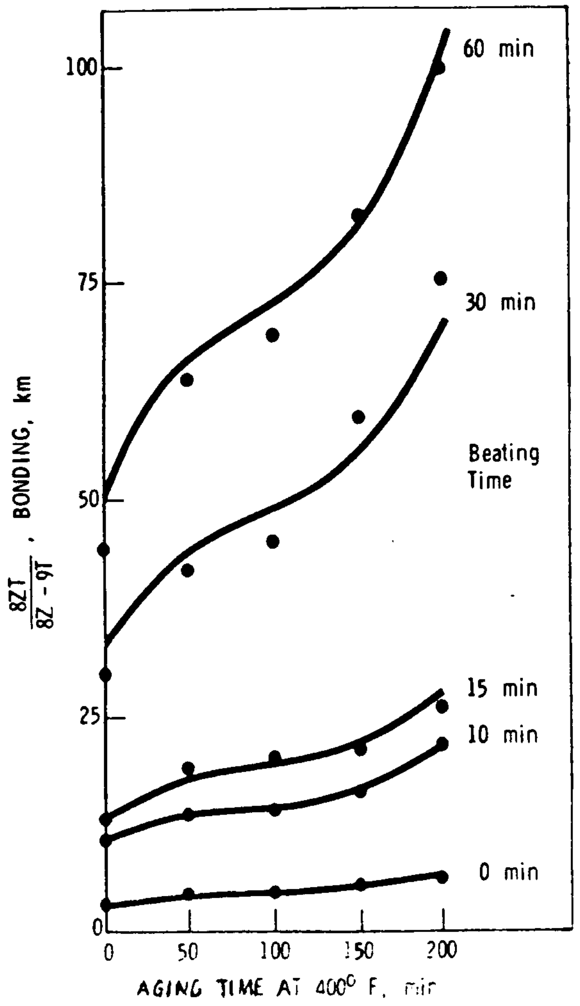

Figure 7.12 Effect of thermal ageing on the fibre bonding strength of sheets made from fibres beaten for different lengths of time. (Page 1969)

The deterioration in fibre strength is therefore to a certain extent compensated for by the improved bond strength and the tensile strength of paper therefore becomes a comparatively insensitive variable for monitoring ageing phenomena in paper. The increased fibre-fibre bond strength can probably be attributed to chemical crosslinking reactions during the thermal ageing (Graminski, 1973; Back and Klinga, 1963).

The fibre-fibre bond strength can in turn be divided into the concept of "specific bond strength" and "bonded area". Changes in the bonded area of paper can be detected through changes in the light scattering coefficient of the paper. When paper ages thermally the light scattering coefficient of the paper does not however change (Luner, 1969), and the conclusion can then be drawn that it is the specific bond strength which increases. During beating of pulp, the bond strength in the sheet increases, primarily because of an increase in the bonded area.

The fold number therefore increases during the beating of pulp and passes through a maximum since the sheet becomes brittle at a high degree of beating. It has for example been shown that during the folding of paper, cracks arise in the film-like material made up of consolidated fine material (fibrils) (Graminski, 1973). Paper with a high degree of beating has a high fines content. Paper which is made from relatively unbeaten fibres has a low fold number, but since the strength properties are dominated by the bond strength in the sheet, the ageing tendency of the sheet can be lower than for a sheet made from a well-beaten stock where the fibre strength dominates the tensile strength of the sheet. The greater bonding surface of the sheet in the latter case increases the crosslinking reactions (cf. fig. 7.12) which leads to a quicker embrittlement.

The conclusion drawn from this analysis is that paper which initially has superior mechanical properties might age quicker and develop poorer properties than a paper which initially has poorer mechanical properties (Luner and Cardwell, 1973).

7f Effect of writing/printing inks

The earliest writing inks consisted of carbon (soot) particles dispersed in water with oils, gum arabic etc. The fact that these inks were not water permanent led to the invention of the water-permanent so-called iron/gallotannin inks already before the birth of Christ. This type of writing ink came to dominate until modern times (Hey 1981). The ink is based on the reaction between green vitriol ($FeSO_4$) and gallotannins. During the reaction, Fe^{2+} forms strong complexes with the phenolic hydroxyl groups in the gallic acid units with the simultaneous formation of H_2SO_4. As dispersion agent, rain water, wine, vinegar etc. are used with gum arabic for consistency (Barrow, 1948). The negative effect of the iron/gallotannin inks on the ageing stability of paper is well documented (see e.g. Hey, 1981) and depends on their acid character in combination with iron as metal catalyser for oxidative attack on the cellulose.

The early printing inks consisted of soot which was dispersed in linseed oil. Before the second world war, most letterpress and lithographic offset varnishes consisted of so-called standard oils which were produced through heating linseed oil so that a suitable viscosity was obtained. These produce water-permanent prints since the oil is self-drying (with unsaturated carbon chains which quickly oxidize). Oxidized, acidic decomposition products of these oils are of course deleterious to the ageing stability of paper.

In the flora of printing methods which exist today (e.g. gravure, flexographs, lithographic offset, letterpress, screen printing, etc.) we limit ourselves in the following summary to the letterpress/offset inks which appear to be the most interesting inks in this context. A modern ink of this type can consist of:

- abietic acid esterified phenolic resin (hardened resin)
- alkyd component (polyester)
- mineral oil (aliphatic, aromatic hydrocarbons with a chain length less than C_{14})
- so-called desiccant (cobalt and manganese salts, ca. 0.1-0.3%)
- pigment (organic colour pigments/soot/inorganic white pigments)

The desiccants are used to catalyse the oxidative drying of the inks.

The organic colour pigments can be benzidine yellow, litholrubin (magenta), phtualocyanine blue (cyan) and the inorganic white pigments can be TiO_2, $Al(OH)_3$ (so called tinting ink) etc. The inks usually consist of 18-20% pigment and 20-30% mineral oil. No sytematic information exists concerning their effect on the ageing stability of paper. The desiccants could possibly be of interest.

More interesting in this context is perhaps the fact that during offset printing, a technique which has grown strongly during the last 20 years, a strongly acid fountain solution with different known and unknown additives is used. Besides surface active substances and metal salts (Al, Cr, Mg etc) they contain high concentrations ($\simeq$ 5%) of phosphoric acid or citric acid. Estimates suggest that this corresponds to an increased acidity of the paper, corresponding to a couple of meq/100 g, i.e. in the same magnitude as the carboxyl group content or buffer capacity of the whole pulp.

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8 COMPARISON BETWEEN NATURAL AND ACCELERATED AGEING OF PAPER

The ageing stability of paper is usually characterized by exposing it to a so-called accelerated ageing procedure. The method is based upon Gösta Hall's early work at the National Institute for Materials Testing.

Empirical studies suggested e.g. that the ageing of paper at 100^{o}C for 72 hours corresponded to between 18 and 25 years of ageing at room temperature (see e.g. Barrow, 1963; Wilson et al 1955).

The equivalence figures are empirical and the ageing also takes place in a dry state which does not correspond to natural ageing at normal atmospheric humidity. In the more scientifically designed method, the paper is aged at several temperatures and a property is measured which can be extrapolated to room temperature (see e.g. Gray, 1969, 1977; Graminski, 1978, 1979; Kelly, 1979; Browning, 1968). The Arrhenius equation is usually used in kinetic ageing studies with the same premises as when it is used in chemical kinetics studies. Chemical kinetics build upon sound physical laws, whereas property kinetic studies build upon empirical relationships.

The difficulties depend on the fact that complex properties such as fold number, tensile strength or brightness cannot be related in a simple way to the chemical composition of the material. Nevertheless, empirical rate constants can be obtained and these rate constants can be related to chemical processes during the accelerated ageing. A physical property, P, which changes monotonously with time is assumed to follow a differential expression similar to that in a rate equation in chemical kinetics. The equation:

$$\frac{dP}{dt} = k_1 f(P) \qquad (1)$$

is a general expression of this kind, where k is a constant and f(P) is a property function which can be integrated. If f(P) were known, an integration would lead to a linear equation:

$$F(P) \equiv \int \frac{dP}{f(P)} = k_1 t \qquad (2)$$

In contrast to a rate equation in chemical kinetics, however, equation 1 has no a priori mechanistic significance and the expression is usually not known. Integration is thus not possible and a search must be made for an empirical function which can linearize the experimental data (P vs. t).

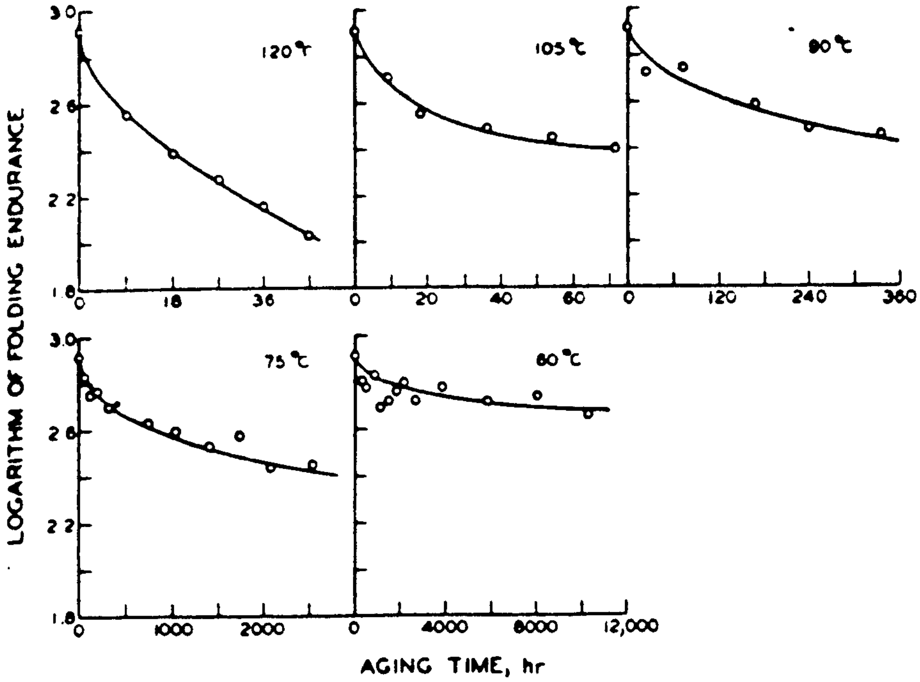

Figure 8.1 Effect of ageing in sealed containers (constant amount of H_2O) at five temperatures on the fold number of paper A2 (Browning and Wink 1968).

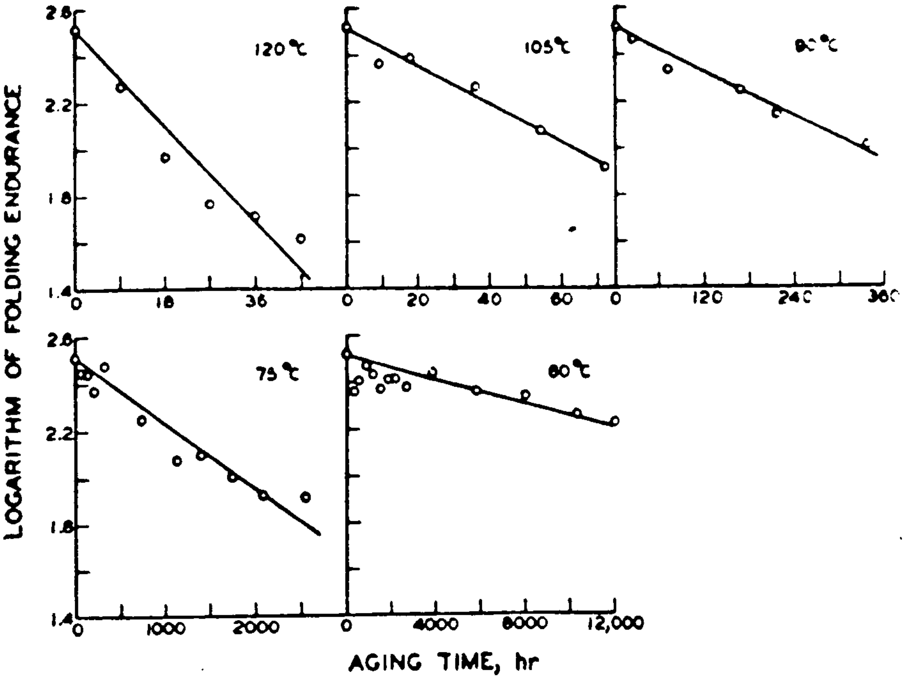

Figure 8.2 Effect of ageing in sealed containers (constant amount of H_2O) at five temperatures on the fold number of paper sample H (Browning and Wink 1968).

Several examples of this kind of property kinetics have been reported in the literature (see e.g. Gray, 1969; Browning, 1968). Browning and Wink found for example in their studies that a logarithmic function linearized fold number data. ($F(P)=\log (P_0/P)$).

Figures 8.1 and 8.2 show how the fold number depends on the ageing time for two different papers. In figure 8.1, the logarithm is not a linear function of the ageing time in contrast to the situation for the paper in figure 8.2 where the logarithm of the fold number is an approximately linear function of the ageing time.

It has similarly been found that other properties such as light absorption coefficient, "zero-span" tensile strength and so on have different linearization functions. Provided a suitable linearization function can be produced, the experiment can be carried out at different temperatures and the rate constant k then obtained can be related to the apparent activation energy, E_a, and the temperature according to Arrhenius' equation:

$$\frac{d\ \ln k}{dT} = \frac{E_a}{RT^2} \qquad (3)$$

In its integrated form the equation becomes:

$$\ln K = \frac{E_a}{RT} + C \qquad (4)$$

where T is the absolute temperature in degrees Kelvin and R is the general gas constant. If ln k is plotted against E_a/T, the activation energy can be calculated from the gradient.

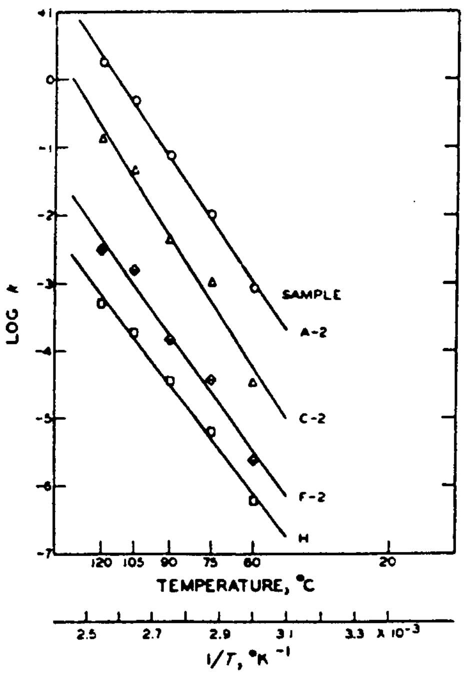

Figure 8.3 *Log k against 1/T for the fold number of samples aged in sealed containers (constant amount H_2O). (The points for sample A2 have been displaced upwards 1 unit, for sample F2 downwards 1 unit and for sample H 2 units downwards) (Browning and Wink 1968).*

Examples of such so-called Arrhenius diagrams are given in fig. 8.3 for some different paper samples.

The activation energy thus calculated varies for different paper samples and is usually between 18 to 36 kcal/mol (Gray 1969 and 1977, Kelly et al 1979). This activation energy can be compared with the activation energy for heterogeneous hydrolysis which also lies between about 18 and 36 kcal/mol (Nelson, 1960).

The so-called Arrhenius relationships are most often linear within the limited temperature range where these have been studied. It is usually not practical to perform accelerated ageing below 60°C.

Table 8.1

Calculated apparent activation energies, kcal/mol (Browning and Wink 1968)

Sample	*Fold number*	*Zero-span tensile strength*	*Specific absorption coefficient*
A2	33.2	28.9	30.4
C-2	35.5	26.9	30.5
F-2	31.4	28.4	30.4
H	29.5	26.7	29.7

The apparent activation energy can also be calculated for other optical or mechanical properties and in table 8.1, for comparison, such calculated activation energies have been compiled for the property kinetics of fold number, "zero-span" strength and light absorption coefficient. (Browning and Wink, 1968).

It can be noted that the apparent activation energy is surprisingly similar for the different property kinetic relationships. With the help of the Arrhenius expression, the expected life-span at 20°C can of course be calculated.

Several publications have directly compared accelerated ageing with natural ageing of paper (Wilson, 1980; Barrow, 1959-1967; Hansson, 1939; Richter and Wells, 1959; Van Royen, 1957; Wilson et al 1955).

Wilson and Parks compared changes in paper properties after 35 years natural ageing with an acclerated ageing (72 hours/100°C) made 36 years earlier on the original samples. In table 8.2, the correlation coefficient and the regression coefficient for the relationship between properties/measurement number after 35 years natural ageing and after accelerated ageing (72 hours/100°C) are listed. There is a relatively good correlation between the properties after 36 years natural ageing and the properties measured after the accelerated ageing. The correlation coefficients are especially high for paper made from waste. It seems probable that for paper made from pure cellulose raw materials such as waste, cotton, the hydrolytic decomposition processes dominate, which also causes the accelerated ageing to have a good correlation with the natural ageing. For paper with a considerable content of hemicellulose and lignin, the oxidative decomposition processes are probably of significant importance.

Table 8.2

Correlation coefficient and regression coefficient for the relationship between different properties/measurement numbers. Ageing after 36 years natural ageing and accelerated ageing (72 hours/100^{o}C) (X = natural ageing; Y = accelerated ageing) (Wilson and Parks 1980)

Property	*Paper type*	*Correlation coefficient*	*Regression coefficient*
α-cellulose content (decrease, %)	*All papers*	0.86	0.49
	Paper of soda/ sulphite pulp	0.88	0.95
	Paper of α-sulphite	0.82	0.29
	Paper of rags	0.97	0.70
Cu-number (increase, absolute)	*All papers*	0.82	0.44
	Paper of soda/ sulphite pulp	0.91	0.62
	Paper of α-sulphite	0.86	0.35
	Paper of rags	0.87	0.72
Fold number (retention, %)	*All papers*	0.63	0.54
	Paper of soda/ sulphite pulp	0.79	0.50
	Paper of α-sulphite	0.83	0.36
	Paper of rags	0.42	0.67
Tearing resistance (retention, %)	*All papers*	0.76	0.62

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9 PAPER CONSERVATION

9a Deacidification methods

Practically all paper conservation methods can be looked upon as deacidification methods, where the aim has been to neutralize acid compounds in the paper and to deposit an alkaline buffer in the paper. Only in recent years has an interest developed into methods based on the reduction of oxidized groups of the cellulose. Good liquid-based deacidification methods for separate pages in books exist today, in contrast to deacidification methods where the base is added in a gaseous state which has several disadvantages such as toxic, explosive gases etc. Table 1 lists some important patents in the deacidification field.

The classic paper conservation method (Schierholtz 1936) is based on treatment of the paper with bicarbonates of alkali earths. There are several variations of these, e.g. Barrow's two-bath method with $Ca(OH)_2$ + $Ca(HCO_3)_2$ treatment etc (Barrow 1959). The soluble calcium ions in the calcium hydroxide solution are precipitated by the hydrogen carbonate ions in the form of calcium carbonate which is deposited in the sheet structure. Because of the higher solubility of $Mg(HCO_3)_2$ than of $Ca(HCO_3)_2$, Mg^{2+}-solutions have been popular (Smith). Old, well-preserved documents often also contain magnesium carbonate and magnesium phosphate (Barrow 1959). The bicarbonate solutions are transformed during drying to the corresponding carbonates. It is also well known that magnesium compounds have an inhibiting effect on the catalytic oxidation of cellulose (Gilbert et al 1973).

Since processes suitable for so-called pulp deacidification can hardly be water-based, different organic media have been tried including gaseous deacidification. $Ba(OH)_2$ dissolved in methanol was tried on an early stage, but the method was abandoned since the cellulose is exposed to alkaline hydrolysis and the barium salts used are poisonous (Baynes-Cope 1969).

The use of organic amines has been investigated in detail (Smith 1966). Barrow Laboratory both investigated and patented the use of morpholine and hexamethylene tetramine in the gaseous state. The hexamethylene tetramine method was abandoned, however, since it was considered too troublesome (Kelly 1980).

Deacidification with morpholine gas (Kusterer 1973, Langwell 1969, Walker 1977) seems to be the most interesting amine-based process since morpholine is non-toxic and is also apparently strongly sorbed to the cellulose (Walker 1977). Even after accelerated ageing at 100°C for 8 days, the paper shows a neutral pH-reaction. Identified disadvantages with morpholine gas are, among others, that it produces colour changes in pyroxylin/leather covers.

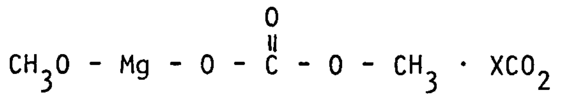
The most frequently mentioned amine process is Langwell's (Langwell 1969, McCarthy 1969) gaseous state process based on the reaction product between cyclohexylamine and carbon dioxide (cyclohexylamine carbonate). The process was abandoned for the reasons previously mentioned.

In summary, it can be established that neither gaseous nor liquid amines function satisfactorily since their volatility from the cellulose is too high and the alkalizing effect is not permanent. Amines also have strong physiological effects and many have a high acute toxicity.

The test with different amines led to a search for new solutions to the problems. R.D. Smith's "The Wei T'O way" (Smith 1977 and 1984) can definitely be included in the modern pulp deacidification methods. The original patent (Smith 1972) is based on magnesium methoxide dissolved in methanol or in Cl-F-hydrocarbons (Freons).

Magnesium methoxide reacts immediately with water and forms methanol (which evaporates) and $Mg(OH)_2$ which reacts further to a complex mixture of bicarbonate, carbonate and hydroxide. The advantage of the method is that the final products are non-toxic and that the final products have a recognized stabilizing effect on the paper. Methanol solutions were, however, found unsuitable and the freon method is preferred.

In the practical use of magnesium methoxide, it became apparent that this was very sensitive to hydrolysis and the handling therefore became difficult because of precipitation. The method was later improved (Kelly et al 1977, Kelly 1976, Smith 1982) by making methoxymethyl magnesium carbonate from magnesium methoxide. Methoxymethyl magnesium carbonate has the formula (Finkbeiner 1963):



$$CH_3O - Mg - O - \overset{\overset{O}{\|}}{C} - O - CH_3 \cdot XCO_2 \qquad (1)$$

Methoxymethyl magnesium carbonate has a considerably higher water tolerance and forms $MgCO_3$ directly during hydrolysis, and $Mg(OH)_2$ formation is avoided, which could be an advantage from an alkaline hydrolysis point of view.

In a supplementary patent (Smith 1972), ethylene oxide treatment of the paper is also included in order to increase the protection against oxidative attack (and the biocidal effect of the ethylene oxide). The deposited magnesium alkoxides catalyse the ethylene oxide reaction with the cellulose.

Richard Smith's "The Wei T'O way" for pulp deacidification is used at the National Library of Canada. The importance of the freons for the thinning of the ozone layer in the atmosphere is of course the subject of continuous discussion and seems to be the only technologically negative argument for the method.

The other modern process for pulp deacidification is the so-called DEZ (D-EthylZinc)-process (Williams 1981, 1976, Kelly 1980). The method builds upon the use of metal organic compounds of the aluminium or zinc alkyl type. Diethyl zinc is especially useful. DEZ reacts immediately with moisture or water and forms $Zn(OH)_2$ with the release of ethene gas. It is therefore important to evacuate the test chamber meticulously so that all moisture is removed before the DEZ-treatment. When DEZ is added to the paper, ethyl zinc cellulosate is formed. Since the alkaline buffer capacity of the paper would exist in the form of ZnO, which can cause photosensitizing and accelerated decomposition of the cellulose, there is an extra final step in the process after the DEZ-treatment. In this final step, 1-3% H_2 (1% by weight of the paper) is first added and then CO_2 in order to convert the zinc compounds to $ZnCO_3$. $ZnCO_3$ does not, however, protect the cellulose against oxidative attack in the same way as magnesium compounds. A clear advantage of the DEZ-process is of course that it takes place in the gaseous state. Several problems (explosion risk, toxicity etc.) seem, however, to be connected with the process (Nyrên 1986) and the reaction product is not an established ageing inhibitor. The final products and their rate of formation in the DEZ-process and in the methyl magnesium carbonate process have not been established and it would be valuable if these were further studied.

Attempts have also been made to dissolve e.g. magnesium or aluminium isopropoxide in super-critical liquids like C_2H_4 or CO_2. Aluminium isopropoxide which dissolved in these liquids did not, however, function as alkaline buffer at extract pH-values in the paper > pH 3. (Kelly 1980).

Lately, the effects of reducing the cellulose with $NaBH_4$ on the ageing stability have also attracted renewed attention (Tang 1981, Gilbert 1973).

A patent application on the treatment of cellulose material with suspensions in air containing microscopic particles of MgO (from calcination of $MgCO_3$) has also been published (Schierholtz 1936). No further information about this work is however available at the time of writing.

Table 9.1

Summary of some deacidification methods.

Schierholtz, O.J.; (1936)	*Ba, Mg^{++}, Sr^{++}, Ca^{++}, HCO_3^- - solution.*	*liquid impregnation (H_2O)*
Langwell, W.H.; (1969)	*Amines e.g.* *Cyclohexyl amine* *Morpholine salts* *carbonates* *acetates etc.*	*liquid impregnation (not H_2O) + VPD (steam state)*
Baynes-Cope, A.B.; (1969)	*$Ba(OH)_2$; MeOH*	*liquid impregnation*
Smith, R.D.; (1972)	*$Mg(OCH)_3$; MeOH or CFn Clm*	*liquid impregnation*
Smith, R.D.; (1982)	*Epoxy magnesium ethyl carbonate*	*liquid impregnation*
Kusterer, J.E.; (1972)	*Hexamethylene tetramine*	*liquid/gas impregnation*
Smith, R.D.; (1972)	*Ethylene oxide/ combination procedure*	*gas*

Kusterer, J.E. et al; (1973)	*Morpholine gas*	*gas*
Walker, B.F. et al; (1974)	*Morpholine gas*	*gas*
Williams, J.C. et al; (1975)	*Precipitation of dissolved salt E.g.* $CaCl_2$+ ($(NH_4)_2CO_3$)	*liquid impregnation*
Kelly, G.B.; (1976)	*Methoxymethyl magnesium carbonate*	*liquid impregnation*
Williams, J.C. and Kelly, G.B.; (1976)	*Diethyl zinc (DEZ)*	*gas*
Tang, L.C. and Troyer, M.A.; (1983)	$NaBH_4$ *+ alkaline soil metals bicarbonates*	*liquid impregnation*
Kundroth, R.A.; (1986)	MgO	*gas disp.*

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