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NATURAL AND ACCELERATED AGEING OF CELLULOSE AND PAPER: A LITERATURE REVIEW.

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ABSTRACT

The various aspects of natural and accelerated ageing of cellulose and paper are presented and discussed. Accelerated ageing constitutes the major methodological tool for the studying of cellulose and paper ageing. The topics include:

- The correlation of natural and accelerated ageing. Methodology of research, results up to date.
- The chemistry of ageing: chain scission, oxidation, crosslinking. Influence of environmental factors (temperature and relative humidity), moisture content, impurities and additives, pH, light, pollution etc.
- The effects on the physicochemical, mechanical, optical and structural properties of cellulose. Changes in water absorption (hornification), porosity and crystallinity.
- The ageing kinetics. Chemical and property kinetics. Courses of ageing under different conditions. Autocatalysis in sealed vessels. Kinetic models. The applicability of the Arrhenius studies for paper permanence predictions and the related controversy are discussed.
- The methods of accelerated ageing. Standards. Dry and humid ageing, sealed enclosures.
- Applications of accelerated ageing: permanence predictions, classification of papers according to their permanence, performance standards for testing for paper permanence, evaluation of paper conservation interventions.

1. INTRODUCTION

Cellulose is a material of high industrial importance with numerous applications; for some of them, permanence and durability¹ are important requirements. Paper is by large the prevalent cellulose product, and paper industry has undergone a remarkable transformation in an endeavor to meet the permanence requirements of the administration, the librarians and the archivists (Stuhrke, 1977; Hagemeyer, 1981; Sclawy and Williams, 1981; Crouse and Wimer, 1991). Kraft paper in oil has been used for cable insulation in electrical transformers and the prediction of an imminent failure is of major importance to the electrical industry (Emsley and Stevens, 1994; Hill et al., 1995a, b; Levchik et al., 1998; Emsley et al., 2000; Ali et al., 2001; Soares et al., 2001; Ding and Wang, 2005; Gilbert et al., 2008). On the other hand, the ageing characteristics of cellulose textile fibres constitute an important concern of the fibre and textile industry and the related branches (Lewin, 1965; Block and Kim, 1986; Burgess, 1986; Cavaco-Paulo, 1998).

Ageing can be defined as the irreversible changes that occur slowly over time (Erhardt and Mecklenburg, 1995), and in the case of paper result in the deterioration of useful properties that can render it unsuitable as an information carrier. The understanding of the ageing of paper and textiles

¹ Permanence: the ability of paper to remain chemically and physically stable over long periods of time. Durability: the ability to resist the effects of wear and tear when in use (Gurnagul et al., 1993; ISO 9706, 1994; ISO 11108, 1996)

requires the study of the ageing of their main component, namely cellulose, and how certain impurities with concentrations ranging from traces to substantial percentages can affect it. These and other relevant subjects have been reviewed in the past by several authors (Padfield, 1965; Gray, 1977; Wilson and Parks, 1979; Hon, 1981; Feller et al., 1986; Fellers et al., 1989; Gurnagul et al., 1993; Emsley and Stevens, 1994; Havermans and Dufour, 1997; Kato and Cameron, 1999a; Porck, 2000; Barański et al., 2005; Strlič et al., 2005a; Strlič et al., 2005b; Zervos and Moropoulou, 2006). In the present review, established views and updates about the various aspects of natural and accelerated ageing of cellulose will be presented and discussed. The topics include the chemistry of ageing, its effects on cellulose properties, the ageing kinetics and the experimental applications, i.e. the methods of accelerated ageing.

The ageing of paper has been in the focus of cellulose chemistry studies because of its chemical and structural complexity, its economic importance but also because it is the substrate which carries the total of the human knowledge. The task of preserving it has been entrusted to the libraries and archives, and paper conservation scientists have studied the influence of the environmental factors on the stability of cellulose. The main process responsible for natural cellulose ageing is the random hydrolysis of the glycosidic linkages between the glucose residues in the macromolecule of cellulose. Oxidation and probably crosslinking also contribute to the deterioration process. It has been shown that the temperature and the relative humidity (RH) of the repositories play a crucial role in the longevity of paper. Pollutants, light, high energy radiation and biological activity (fungi, bacteria and pests) were also found to exert a detrimental effect on paper. Studies have shown that the acidity of paper is the most important internal factor that accelerates significantly the decomposition of cellulose and that transition metal ions and other additives and impurities contribute to it. Lignin, a remnant of the raw plant material in paper, which was also believed to considerably contribute to the deterioration of paper, was proved to exert a protective influence on cellulose due to its antioxidant properties. It has also been shown that the higher the accessibility (and the lower the crystallinity) of cellulose, the higher the susceptibility to ageing. Ageing reduces the degree of polymerization (DP) and deteriorates the mechanical and optical properties of cellulose and paper. The chemistry and the effects of degradation on paper and cellulose properties will be discussed in detail in the next chapters.

The study of the natural ageing of cellulose and all the related subjects, i.e. the question of permanence of cellulose products such as paper and the results of various processes on it, present the insurmountable obstacle that the effects of natural ageing at ambient conditions can take several years to register on certain cellulose properties, and even several decades to produce statistically significant changes. The method to overcome this problem is the application of hostile environments which are far more aggressive than the normal environment paper and cellulose are exposed to. The first and the most widespread approach was the exposure to elevated temperatures, usually referred to as thermal accelerated ageing tests. Indeed, most of the current knowledge concerning the effects of ageing on cellulose has been acquired by accelerated ageing. Accelerated ageing at elevated temperatures in general has a sound theoretical base on the Arrhenius equation, but in the case of paper and cellulose, due to the complexity of the materials and the chemistry of degradation, many objections have been expressed. The controversy has focused on the question of whether artificial ageing produces the same effects as natural ageing at an accelerated rate, or introduces other chemical reactions that do not occur at natural ageing and what the conditions of ageing (temperature, relative humidity, closed or open environments) should be to guarantee such a result. It has also been questioned whether elevated temperature accelerates the various interdependent reactions that bring about the natural ageing of cellulose at the same rate, or disturbs the equilibrium among them, producing spurious results (Arney and Jacobs, 1979, 1980; Bansa and

Hofer, 1989; Bansa, 1992; Erhardt and Mecklenburg, 1995; Porck, 2000; Shahani et al., 2001; Bansa, 2002). Another matter of controversy related to the above is the applicability of the Arrhenius law to the study of the change of certain mechanical, chemical and physicochemical properties of cellulose, which deteriorate with ageing, for paper permanence predictions (Baer and Indictor, 1977; Erhardt et al., 1987a; Strofer-Hua, 1990; Erhardt and Mecklenburg, 1995; Zou et al., 1996a; Shahani et al., 2001). All these matters will be addressed in the following discussion.

The temperature domain of thermal accelerated ageing starts from ambient temperatures and reaches up to 105°C. Nevertheless, results from higher temperature treatments will be reported here when relevant, especially concerning the kinetic models of cellulose degradation. The experimental setup varies from arid ovens to humid ovens and sealed vessels. Artificial ageing has also been achieved by other hostile environments, such as polluted atmospheres or exposure to light. These ageing tests have been conceived in order to examine the resistance of paper and cellulose to pollution and light, which are important factors of paper degradation kept in libraries and archives. In this review, the focus will be on thermal accelerated ageing, with few references concerning other types of ageing.

2. ACCELERATED VS NATURAL AGEING

The attempts to compare the results of natural and accelerated ageing of paper and find parallels between them fall in one of the following three categories: comparison of properties, Arrhenius studies and comparison of products.

Comparison of properties. Parallel studies of natural and accelerated ageing and comparison of their effects on certain mechanical and chemical properties of the test papers. Attempts were made to determine the ratio of durations of accelerated ageing and natural ageing that produce the same effect. This approach was the first undertaken in chronological order.

In 1928, the National Bureau of Standards of the U.S.A. (N.B.S.) tested a group of writing rag and wood pulp papers before and after accelerated ageing at 100°C for 72 hours and stored more samples of those papers for future testing in order to compare the results of natural and accelerated ageing (Wilson and Parks, 1983). Samples of those papers were tested after 4 and 8 years of natural ageing. The determination of the chemical properties of the samples (pH, water-soluble acidity, α - β - and γ -cellulose content and copper number) was repeated (Wilson et al., 1955) after 22 years and of the mechanical properties (folding endurance and tensile strength) after 26 years. The results indicated a fair correlation between natural and accelerated ageing, but quantitative conclusions could not be drawn. The correlation was studied by means of statistical analysis of the folding endurance results and indicated a rough correspondence between the results of 24 hours of accelerated ageing at 100°C and 6-8 years of natural ageing. A second study (Wilson and Parks, 1983) included a group of 18 papers made in the experimental machine of the N.B.S., consisting of rag, 50-50 soda-sulfite and purified wood-pulp fibres. The papers were tested in 1937 and tested again after 36 years. It was concluded that pH and changes in α -cellulose content, copper number and tearing resistance after accelerated ageing for 72 hours at 100°C were reasonable indications of stability. The analysis of the results showed a good correlation between changes in alpha cellulose and copper number and a fair correlation between changes of folding endurance and tearing resistance caused by natural and accelerated ageing, indicating that accelerated ageing correlates well enough to natural ageing, bearing in mind the limitations of accelerated ageing tests. When those results were compared to the results of accelerated ageing of hand sheets at 90°C and 0% and 50% RH, it was concluded that an accelerated ageing atmosphere should contain some moisture.

The credibility of the accelerated ageing tests has been questioned by Bansa (Bansa and Hofer, 1989; Bansa, 1992, 2002). He has presented a plethora of plots of many different properties of various types of paper against the duration of ageing and commented on the very different and unpredictable shapes of the diagrams. He believes that these differences show that the various interdependent reactions that comprise what is collectively called “accelerated ageing” are very different for papers of various origins, composition (different cellulose content and different impurities and additives) and history. He suggests that no method of accelerated ageing can affect every kind of paper in the same way and that the results of accelerated ageing can be totally misleading. He concludes that there is no correlation between natural and accelerated ageing and advises caution in the interpretation of its results. Nevertheless, he accepts the use of accelerated ageing for determining if a process (i.e. an innovation in the production or a paper conservation intervention) can improve or deteriorate the ageing rate of a specific paper.

In another study, Zou et al. (1996b) compared their predictions based on the Arrhenius equation (Zou et al., 1996a) to the results of natural ageing for 22 years of lignin-free paper, and found a good correlation between natural and accelerated ageing. The comparison was between rate constants predicted from Arrhenius studies based on inverse DP for the artificially aged samples and those calculated from inverse DP for the naturally-aged samples.

Arrhenius studies. Kinetic studies of paper and cellulose properties (mainly folding endurance, brightness and inverse DP) at various elevated temperatures with subsequent Arrhenius studies, in order to examine the linearity of the Arrhenius plots. The linearity of the plots indicates the applicability of the Arrhenius equation in the temperature range studied. By extrapolating the Arrhenius plots to ambient temperatures, the rate constants at ambient temperatures are determined, which are considered to be equal to the natural ageing rate constants. This methodology is based on the assumption that no change in the mechanism of the degradation reactions takes place between the lowest temperature studied and the ambient temperature. This underlying assumption is often stressed in the relevant literature (Kaminska et al., 2001; Shahani et al., 2001), but sometimes is taken for granted.

The linearity of the Arrhenius plots, either for physical property kinetics or for studies of the inverse DP, has generally been established (Browning and Wink, 1968; Gray, 1969; Shafizadeh and Bradbury, 1979; Roberson, 1981; Emsley and Stevens, 1994; Zou et al., 1996a; Kaminska et al., 2001; Shahani et al., 2001) with few exceptions (Browning and Wink, 1968).

It has been shown (Arney and Jacobs, 1979; 1980) that the ageing of a newsprint and of a rag paper at 90°C is mainly the result of two competing reactions, one oxygen-dependent (atmospheric oxidation) and the other oxygen-independent. The relative contribution of these reactions was found to be different at different temperatures between 60 and 120°C and depended on the type of paper, the humidity and the monitored property. It was concluded that accelerated ageing tests at temperatures around 100°C could lead to wrong conclusions about the chemical processes responsible for paper ageing at room temperature. Nevertheless, the authors suggested that although the mechanism of the degradation was temperature-dependant, the Arrhenius plots could still be used for relative permanence prediction since they were linear in all cases. They agree with the opinion expressed by other researchers (Gray, 1969; Graminski et al., 1979) that single-temperature ageing tests cannot properly rank papers according to their permanence.

Erhardt and Mecklenburg (1995) have pointed out that the study of the properties of paper and of the manner they are affected by ageing does not allow for the comparison between two different conditions of ageing, because the different reactions involved have similar activation

energies and the Arrhenius study does not reveal the details of the mechanism. On the contrary, the complex system reacts as if one single mechanism exists and the activation energy determined has an intermediate value. In order to avoid the uncertainties caused by the study of any individual property, they chose to study the concentration of the products of individual reactions. Thus, they followed the concentration of glucose and certain glucose oligomers and found a linear dependence between the natural logarithm of them and time of degradation for the initial phase of ageing. The Arrhenius studies based on the calculated rate constants gave values of E_a for glucose and glucose oligomers ranging from 92 to 100 KJmol^{-1} .

Zou et al. (1996a) analyzed theoretically the application of the Arrhenius equation on complex systems with multiple simultaneous reactions with different activation energies and concluded that “the accelerated ageing test using the empirical Arrhenius procedure has a potential to predict natural ageing behavior if factors affecting the frequency factors of each reaction, such as moisture content, hydrogen ion concentration, oxygen content, etc. are kept the same between natural ageing and accelerated ageing”

Comparison of products. Studies of the compounds produced by natural and accelerated ageing. The rationale behind this approach is that similar reactions produce similar products. If natural and accelerated ageing involve identical chemical processes in the same proportions, than their products must be identical and in similar proportions.

Erhardt et al. (1987a) proposed that different conditions of ageing should be compared by comparing the distribution of the degradation products and that this is how the correlation between natural and artificial ageing should be examined (Erhardt, 1993; Erhardt et al., 1999). By this methodology, it was concluded that the ageing process (that is, the contribution of various individual reactions) is mainly a function of relative humidity, while the ageing rate is determined mainly by temperature. It was also shown that the ageing process in the range of 60-90°C and 30-80% RH is relatively uniform, while dry ageing produces quite different results (Erhardt and Mecklenburg, 1995).

Using the same principle, Shahani et al. (2001) compared accelerated ageing to natural ageing. Two methods, ion chromatography and capillary electrophoresis were used for the comparison of the products of natural ageing and accelerated ageing. It was found that the two modes of ageing produced the same products at about the same proportions. From the three methods of ageing tested, ageing in sealed tubes was proved to bear the most resemblance to natural ageing. Sealed tubes served two objectives: first, they maintained the moisture content of paper equal to that at ambient conditions and second, they retained the acidic volatile degradation products of ageing, causing further acceleration of the process. These findings were further confirmed by others (Dupont et al., 2007). The author of the present review believes that the establishment of the correlation of accelerated ageing to natural ageing by the “ASTM/ISR Research Program on the Effects of Aging on Printing and Writing Papers” (Shahani et al., 2001) is one of the most important breakthroughs of the last years concerning the ageing of paper and cellulose. As part of the same program, a long-term study of the results of natural ageing was launched. 15 libraries agreed to hold large quantities of the sample papers examined so far in book form, which are scheduled for testing every 10 years for the next 100 years. The results will be used to improve the correlations of the accelerated ageing data with natural results, and will hopefully resolve most if not all of the remaining issues.

3. THE CHEMISTRY OF AGEING

The chemistry of ageing has been determined in detail by accelerated ageing experiments and confirmed to a certain degree by studying naturally aged paper and cellulose. Parallel studies of natural and accelerated ageing have also been conducted and the results on the properties of paper and the products of both modes of ageing have been compared (Wilson et al., 1955; Barrow and Sproull, 1959; Wilson and Parks, 1979; Wilson and Parks, 1980; Roberson, 1981; Wilson and Parks, 1983; Barrett, 1989; Erhardt, 1993; Zou et al., 1993; Zou et al., 1996b; Brandis and Lyall, 1997; Shahani et al., 2001; Lattuati-Derieux et al., 2006; Dupont et al., 2007). It has been established that the predominant degradation route in the dark and at mild environmental conditions is that of hydrolysis, with a potential synergism of oxidation and probably a contribution from crosslinking. These three routes have also been reported to bring about the ageing of cellulose during thermal accelerated ageing (Roberson, 1976; Graminski et al., 1979; Wilson and Parks, 1979, 1983). Fellers et al. (1989) speculated that physical ageing² may also contribute to the embrittlement of paper and cellulose. The acidity of paper has been identified as the most important intrinsic factor that promotes the ageing of paper. Various additives and impurities contribute to the susceptibility to ageing. Light and pollution accelerate the natural ageing of paper, along with elevated temperature and high relative humidity.

3.1. DEGRADATION PRODUCTS

The degradation of cellulose and paper produces a large number of compounds which originate from the hydrolysis and oxidation of cellulose, but also from the degradation of hemicelluloses and lignin. The products of degradation can be classified in four categories, according to the compound class, its origin and method of identification:

- Simple sugars and cellulose oligomers: The main products of paper degradation include glucose, cellulose oligomers with DP up to 10 (mainly cellobiose, cellotriose and cellotetraose) and arabinose, xylose, mannose and galactose, which originate from the hydrolysis of cellulose and hemicelluloses and were identified as products of both natural and accelerated ageing (Erhardt et al., 1987a; Erhardt and Mecklenburg, 1995; Erhardt et al., 1999; Shahani et al., 2001; Dupont et al., 2007; Stephens et al., 2008). Their identification was accomplished by gas chromatography (Erhardt et al., 1987b; Erhardt and Mecklenburg, 1995), ion chromatography (Shahani et al., 2001), capillary zone electrophoresis (Dupont et al., 2007) and electrospray ionization-mass spectroscopy (ESI-MS) (Stephens et al., 2008).
- Aliphatic organic acids: They are determined from the water extracts of naturally or artificially aged paper by capillary electrophoresis (Shahani et al., 2001; Dupont et al., 2007). They include acetic, formic, oxalic, lactic, glycolic, succinic and malic acids (Shahani et al., 2001; Shahani and Harrison, 2002; Lattuati-Derieux et al., 2006; Dupont et al., 2007). Their mechanism of formation has not been determined in detail, but they are considered as products of the combined action of hydrolysis and oxidation (Lattuati-Derieux et al., 2006).
- Phenolic products of lignin degradation: They have been determined by capillary electrophoresis (Shahani et al., 2001; Dupont et al., 2007) of methanol or water extracts

² Physical ageing is a process pertaining to the amorphous and semicrystalline polymers, characterized by a decrease in volume with time, which affects the mechanical properties and causes embrittlement of the polymer (Struik, 1978).

of aged paper. Some of them are: vanillin, vanillic acid, 4-hydroxy benzoic acid, 4-hydroxy benzaldehyde, 4-hydroxy acetophenone, ferulic acid, acetpsyringone, acetovanillone.

- Volatile organic compounds (VOCs), determined from the ambient atmosphere of aged paper by gas chromatographic-spectroscopic (GC-FID and GC-MS) and gas chromatographic-olfactory (GC sniffing technique) techniques (Buchbauer et al., 1995), high performance liquid chromatography (HPLC) (Levchik et al., 1998) or headspace-solid-phase microextraction (HS-SPME) coupled with gas chromatography and mass spectrometry (GC/MS) (Lattuati-Derieux et al., 2006). Compounds classified in other categories such as volatile aliphatic acids and lignin degradation products are also determined together by those methods. VOCs include: acetic acid, toluene, butanoic acid, furfural, ethylbenzene, xylene, pentanoic acid, heptanal, benzaldehyde, phenol, acetophenone, vanillin, guaiacol, various alkanes and higher aliphatic acids and aldehydes. Furfural, furoic acid and other furanic derivatives have been classified either as lignin degradation products or as cellulose or hemicelluloses hydrolysis and oxidation products (Emsley and Stevens, 1994; Levchik et al., 1998; Shahani et al., 2001; Lattuati-Derieux et al., 2006; Dupont et al., 2007). Methanol production has also been reported from the ageing of kraft paper in transformer oil (Gilbert et al., 2008).

3.2. ACID HYDROLYSIS AND CHAIN SCISSION

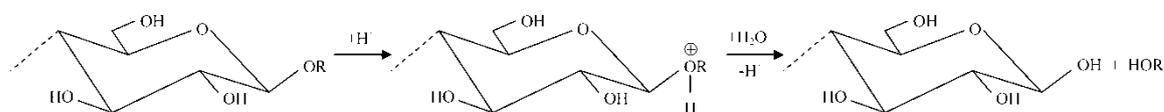


Fig. 1: Acid-catalyzed hydrolysis of cellulose

The prevalent deterioration reaction responsible for the natural and accelerated ageing of paper and cellulose is the acid hydrolysis of the glycosidic bonds between the glucose moieties of the cellulose macromolecule (Fig. 1) (Barrow and Sproull, 1959; Roberson, 1976; Wilson and Parks, 1979; Fellers et al., 1989; Gurnagul et al., 1993; Zou et al., 1994; Barański et al., 2005). Zou et al. (1994) studied the effects of accelerated ageing at various relative humidities on pure cellulose paper of low pH and DP. Their results indicated that the loss of strength and the developed brittleness were due to the loss of fibre strength, resulting from the acid-catalyzed hydrolysis of cellulose and not bond strength loss. Molecular mass distributions derived from size exclusion chromatography experiments suggested that the chain scission occurs at random positions. Whitmore and Bogaard (1994) showed that during the dry or humid oven-ageing of paper, the ratio of produced carbonyls to scissions remains constant and about equal to 1 and that no detectable carboxyls are produced, indicating thus that hydrolysis is by far the main degradation route during thermal accelerated ageing. This was further corroborated by studying the main products of cellulose and paper degradation (Erhardt et al., 1999). Deacidification, that is the treatment of acidic paper with various mildly alkaline agents, has been proved to significantly reduce the degradation rate and is a widely practiced stabilization strategy (Barrow and Sproull, 1959; Kelly et al., 1977; Smith, 1977; Walker, 1977; Kelly and Fowler, 1978; Hey, 1979; Tang, 1981; Wilson et al., 1981; Mihram, 1986a; Mihram, 1986b; Calvini et al., 1988; Morrow, 1988; Smith, 1988; Bredereck et al., 1990; Daniel et al., 1990; Lienardy and Van Damme, 1990; Green and Leese, 1991; Lienardy,

1991; McGee, 1991; Vallas, 1993; Brandis, 1994; Hanus, 1994; Lienardy, 1994; Stroud, 1994; Wittekind, 1994; Guerra et al., 1995; Havermans et al., 1995; Liers and Schwerdt, 1995; Shahani and Hengemihle, 1995; Kolar and Novak, 1996; Middleton et al., 1996; Stauderman et al., 1996; Bansa, 1998; Bukovsky, 1999; Moropoulou et al., 2001; Dupont et al., 2002; Cheradame et al., 2003; Rousset et al., 2004). In acidic paper, hydrolysis is catalyzed by acids, but under neutral and alkaline conditions the mechanism of degradation is complex and oxidation seems to play an important role (Margutti et al., 2001). Nevertheless, it has been shown that chain scission in general is the main pathway of cellulose degradation regardless of the molecular mechanism of the reaction and the cause of deterioration and that it occurs in the cases of photochemical, photolytic, thermal and enzymatic degradation (Shafizadeh and Bradbury, 1979; Feller et al., 1986; Emsley and Stevens, 1994; Whitmore and Bogaard, 1994; Havermans and Dufour, 1997; Kolar et al., 2005). The immediate effect of hydrolysis and chain scission is the reduction of the degree of polymerization, which can be quantified either by measurements of the intrinsic viscosity of cellulose solutions or by size exclusion chromatography (SEC) (Zou et al., 1994; Hill et al., 1995a; Emsley et al., 2000; Jerosch et al., 2002; Dupont et al., 2007). In earlier studies, the increase in alkali solubility was used to follow hydrolysis (Graminski et al., 1979; Wilson and Parks, 1979). The existence of carbonyls, with or without ring opening, on the cellulose chain at random positions enhances the sensitivity of the adjacent glycosidic bonds and the overall liability to acid hydrolysis (Ivanov et al., 1961). It has been shown that at the early stages of deterioration, chain scission occurs at random positions of the amorphous cellulose areas, while later the process becomes progressively less random (Stephens et al., 2008). The kinetics of hydrolytic degradation is discussed in a next chapter.

The acidity of paper may originate from various sources (Barański et al., 2005):

- From the hydrolysis of metal ions³: Al³⁺ ions from alum (K₂SO₄.Al₂(SO₄)₃.24H₂O) or papermakers alum (Al₂(SO₄)₃.18H₂O), which were used mainly for the precipitation of rosin (Gurnagul et al., 1993; El-Saied et al., 1998, 2000; Barański et al., 2005). Fe³⁺ produced by oxidation of the Fe²⁺, which in the form of FeSO₄ is a component of the iron-gall ink, the most common hand-writing ink from the 9th to the early 20th century in Europe and its colonies (Van Gulik and Kersten-Pampiglione, 1994; Neevel, 1995; Banik, 1997; Metz, 1997; Reissland, 1999; Sistach et al., 1999; De Feber et al., 2000; Kolar and Strlic, 2004; Kolar et al., 2007; Potthast et al., 2008). Sulfuric acid, another component of iron-gall ink, may also contribute to the acidity of paper.
- From the products of ageing. This source of acidity has been underestimated, but recent studies indicate its importance (Shahani et al., 2001; Shahani and Harrison, 2002; Zervos and Moropoulou, 2005; Lattuati-Derieux et al., 2006). Carboxyls may also be present in acidic hemicelluloses or produced by oxidative bleaching during paper production.
- From atmospheric pollution (Hudson, 1967a; Baer and Berman, 1986). Pollutants that contribute to the acidity of paper include sulfur dioxide (SO₂), which can be oxidized to sulfur trioxide (SO₃) and form sulfuric acid (H₂SO₄) in the presence of moisture and

³ Metal ions react with water and form solvated ions [M(H₂O)_x]^{v+}, which act as proton donors (Brønsted-Lowry acids) and are hydrolyzed according to the equation (Hatzioannou, 1978, p. 133; Roberts, 1996, p. 125; Barański et al., 2005): [M(H₂O)_x]^{v+} + H₂O ↔ [M(H₂O)_{x-1}(OH)]^{(v-1)+} + H₃O⁺. The acidic nature of Fe³⁺ and Al³⁺ ions is evident from the fact that the pH values of 0.1 N solutions of them is 2.05 and 2.99 respectively (Hatzioannou, 1978, p. 354).

nitrogen oxides (NO_x), which have been proved to be the most aggressive of all (Reilly et al., 2000). Ozone and various VOCs can oxidize cellulose and other paper components to acidic compounds (Daniel et al., 1990; Herrera, 1990; Havermans, 1995; Hofenk de Graaff et al., 1996; De Feber et al., 1998; Begin et al., 1999; Havermans and Steemers, 2005).

- From the migration of acidic substances from neighboring packaging materials, furniture and acidic paper and cardboard (migration effect) (Slavin and Hanlan, 1992; Tetreault and Stamatopoulou, 1997; Bulow et al., 2000; Carter et al., 2000).
- From the acidic metabolic products of the microorganisms and biological agents that feed on paper and the other organic materials present in libraries and archives (Szczepanowska, 1986; Florian, 1996; Gallo et al., 1998; Valentin et al., 1998; Florian and Manning, 1999; Ricelli et al., 1999; Nitterus, 2000; Rakotonirainy et al., 2003; Buzio et al., 2004).

3.3. OXIDATION

As discussed above, the results of Whitmore and Bogaard (1994) indicate that during thermal ageing and in both humid and arid ovens, the degradation of pure cellulose paper is strictly hydrolytic, with no detectable contribution from oxidation. Zou et al. (1994) reached the same conclusion for acidic cotton cellulose paper by comparing the rate of chain scission under oxygen and nitrogen. Nevertheless, other authors have found that the contribution from oxidation is not negligible, especially for neutral or alkaline paper (Major, 1958; Roberson, 1976; Arney and Jacobs, 1979; Wilson and Parks, 1979; Arney and Jacobs, 1980; Arney and Novak, 1982; Fellers et al., 1989; Gurnagul et al., 1993). For example, Arney and Jacobs (1979, 1980) and Arney and Chapdelaine (1981) reported that the ageing of a newsprint and of a rag paper is the result of two competing reactions, one oxygen-dependent (atmospheric oxidation) and the other oxygen-independent with different relative contribution at different temperatures that depended on the type of paper, the humidity and the monitored property. Although these results seem to contradict Whitmore and Bogaard's, one should consider that Whitmore and Bogaard compared the functional groups (carbonyls and carboxyls) created by ageing with the chain scissions, while others compared the rates and the extent of ageing in oxygen and nitrogen atmospheres (Major, 1958; Arney and Jacobs, 1979, 1980; Arney and Novak, 1982). In the first case, what Whitmore and Bogaard proved was that no extra carbonyls or carboxyls were produced compared to what was expected from the measured scissions, not that the scissions were not, at least partly caused by oxidation. If oxidation had occurred, it may have promoted chain scission but have left no measurable functional group residue on cellulose backbone. In the second case, it was proved that the presence of oxygen can promote chain scission. Therefore, these results are compatible if oxidation leads to the cleavage of glycosidic bonds and the remainder of the oxidized groups on the cellulose backbone depends on the conditions of ageing and on the paper composition. They also indicate that pure cellulose paper is less susceptible to oxidation than paper containing lignin, hemicelluloses and additives. The experimental results of various authors indicate that these are plausible explanation of this seeming contradiction. In fact, it has been shown without any doubt that oxidized cellulose degrades faster than normal cellulose (Ivanov et al., 1961; Whitmore and Bogaard, 1995; Margutti et al., 2001; Calvini et al., 2004; Strlič et al., 2005a; Calvini et al., 2006) and Arney and Chapdelaine (1981) have speculated on the existence of a mechanism of acid-sensitive oxidation. Apart from that, in Golova's paper (Golova and Nosova, 1973), the mechanism of degradation of oxidized cellulose presented in the first figure in page 329 results in two new cellulose ends with one new carbonyl each (glycosidic bond cleavage with no production of extra carbonyls). One should also bear in

mind that a part of the oxidized functional groups are on fragments that are volatile and are lost in the environment (see above) (Wilson and Parks, 1979). Oxidation was monitored in the early studies by following the copper number (Graminski et al., 1979), but recently chemiluminescence studies are employed (Rychlý and Rychlá, 2005; Strlič et al., 2005a; Strlič et al., 2005c). The Russell effect has also been used for the studying of cellulose and paper oxidation (Daniels, 1984; Daniels, 1986; Caverhill et al., 1999).

Oxidation during thermal accelerated ageing is brought about by the action of oxygen (autoxidation). The atmospheric oxygen acts as a non-specific oxidizing agent (Major, 1958), not directly⁴ but via various complex mechanisms, possibly by converting terminal or other existing carbonyls to peroxides (Strlič et al., 2005a), thus producing new carbonyls and carboxyls, with or without ring opening. Three alternative mechanisms have been proposed for the oxidation of cellulose in alkaline conditions, a radical chain, an ionic and an ion-radical chain mechanism, with the superoxide (HOO^\bullet or $\text{O}_2^{\bullet-}$), the hydrogen peroxide (H_2O_2) and the hydroxyl radical (HO^\bullet) playing an important role (Golova and Nosova, 1973; Kolar, 1997; Strlič et al., 2005a). Oxidized cellulose degrades fast by acid hydrolysis (Ivanov et al., 1961) or under alkaline conditions (Kolar, 1997; Malesic et al., 2002; Strlič et al., 2005a) due to β -alkoxy-elimination (Graminski et al., 1979; Fellers et al., 1989; Bicchieri and Pepa, 1996; Dupont, 1996a; Calvini et al., 2004; Calvini et al., 2006). The reaction starts with the abstraction of a hydrogen atom bound to a carbon by a hydroxyl radical. A hydroxyalkyl radical is produced and converted by oxygen to the corresponding carbonyl structure, with the alkoxide at a β position to the carbonyl. An adjacent H^+ is then abducted by a OH^- and a carbanion is produced, which is stabilized by a charge shift and the cleavage of the glycosidic bond (Fig. 2).

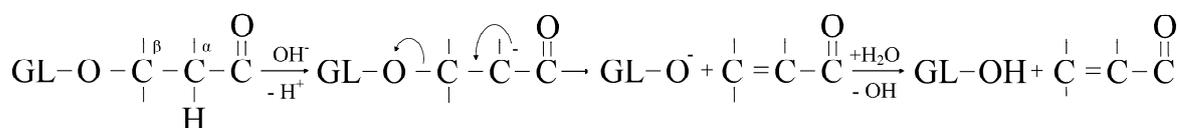


Fig. 2: β -alkoxy-elimination

The treatment with reducing agents like sodium borohydride that convert carbonyls to hydroxyls has been found to decrease the degradation rate of oxidized cellulose (Block and Kim, 1986; Tang, 1986; Lehtaru and Ilomets, 1997).

Transition metal ions contribute significantly to the oxidative process by reducing oxygen to superoxide and by producing more reactive radicals (Shahani and Hengemihle, 1986, 1995; Bicchieri and Pepa, 1996; Kolar, 1997; Calvini and Gorassini, 2002a; Strlič et al., 2005a; Calvini and Silveira, 2008; Potthast et al., 2008):



Other impurities and additives such as lignin and hemicelluloses may play a part in the oxidation of cellulose by reacting with oxygen and initiating the production of reactive oxygen species and peroxides (Kolar, 1997; Strlič et al., 2005a). Although lignin was considered to promote paper degradation, it has been demonstrated that it exhibits an antioxidant effect and stabilizes cellulose against thermal accelerated ageing but also against natural ageing, affecting negatively only the

⁴ A direct reaction between oxygen in the ground state and cellulose is forbidden due to spin restrictions (Kolar, 1997; Strlič et al., 2005a).

optical properties of paper (Hon, 1975c; Zou et al., 1993; Schmidt et al., 1995; Begin et al., 1998). Light exposure catalyzes the oxidation of paper (see below).

3.4. CROSSLINKING

During the thermal ageing of cellulose, auto-crosslinking of the cellulose chains occurs, which results in the increase of the wet-strength, the decrease of the wet elongation, the restriction of the swelling by water sorption and the increased brittleness of paper (Ruffini, 1966; Back, 1967; Graminski, 1970; Wilson and Parks, 1979). Crosslinking is speculated to occur also during natural ageing (Graminski, 1970; Roberson, 1976). Back (1967) reported an increase of the wet-strength up to 40-50% of the dry strength after heating for about 2 weeks at 70°C, about 2 minutes at 200°C and a few seconds at 350°C. The linearity of the Arrhenius plots indicated that the mechanism of the reaction did not change over the range of the temperatures studied (70-350°C). The Arrhenius studies yielded activation energies between 20 and 30 Kcal/mol, depending on the property used for the study of crosslinking. The proposed mechanisms suggest the oxidative production of carbonyls on neighboring chains and the formation of hemiacetal bonds between them (Back, 1967), or the formation of ester linkages between carboxyl in one chain and hydroxyl in a neighboring chain (Ruffini, 1966). The reaction is catalyzed by acidity and metal ions with high redox potential. The reported by many authors increase of the tensile strength at the initial stage of thermal ageing may be attributed to crosslinking (Green and Leese, 1991, p. 154; Cernic Letnar and Vodopivec, 1997, p. 80; Bansa, 1998, p. 19; El-Saied et al., 1998, p. 166; Nada et al., 1999, p. 36; Zervos, 2007c, p. 271). Crosslinking and chain scission are competing processes, thereby tensile strength goes through a maximum and then declines.

4. FACTORS AFFECTING THE AGEING PROCESS

4.1. TEMPERATURE

The temperatures used for accelerated ageing range between ambient temperatures and 105°C. Higher temperatures have been used occasionally and are specified in various standards for special purposes, but they are not considered good practice for general testing (Barrow and Sproull, 1959; Arney and Jacobs, 1979, 1980; Strofer-Hua, 1990), since the higher the temperature, the more uncertain becomes the extrapolation to ambient conditions. Arney and Jacobs (1980) found that the relative contribution of the oxygen-independent and the oxygen-dependent degradation was a function of temperature and suggested that the higher the temperature, the more different was the mechanism of degradation from the ambient conditions. In addition, it has been suggested that the rate of degradation changes notably above 140°C (Yoshida et al., 1987; Emsley and Stevens, 1994) and that at higher temperatures the contribution from pyrolysis may become a considerable factor. Another issue precluding temperatures higher than 100°C is the difficulty to control relative humidity at those temperatures (Graminski et al., 1979). There is no lower temperature limit, but the need for practically applicable tests demands short duration of ageing and therefore the highest possible temperatures. The most common temperatures used are 80°C and 90°C for humid ageing and 100°C and 105°C for dry ageing (ISO 5630-2; TAPPI T 453; ISO 5630-1; ISO 5630-3).

The well-known “rule of thumb” that an increase in temperature of 10°C results in the doubling of the degradation rate does not seem to apply for paper degradation (Erhardt, 1989; Erhardt and Mecklenburg, 1995; Porek, 2000). Instead, the diverse values of the activation energy determined for paper degradation (20-30 Kcal/mol) give various temperature values that correspond to a doubling in degradation rate, lower than the 10°C mentioned above and probably as low as 5°C. Nevertheless, the accuracy of the Arrhenius tests is not sufficient to produce quantitative

correspondence factors between temperatures and ageing times (Browning and Wink, 1968). The matter is addressed in detail elsewhere in this review.

In order to slow down the deterioration process, the temperature at the storage areas in libraries, archive and museums where paper is kept should be maintained as low as possible, considering the cost and the impact on the building. Standards suggest temperatures under 20°C (AS 4390, 1996), but recently even lower temperatures have been proposed (temperature range 16-19°C, BS 5454, 2000).

4.2. RELATIVE HUMIDITY - MOISTURE CONTENT

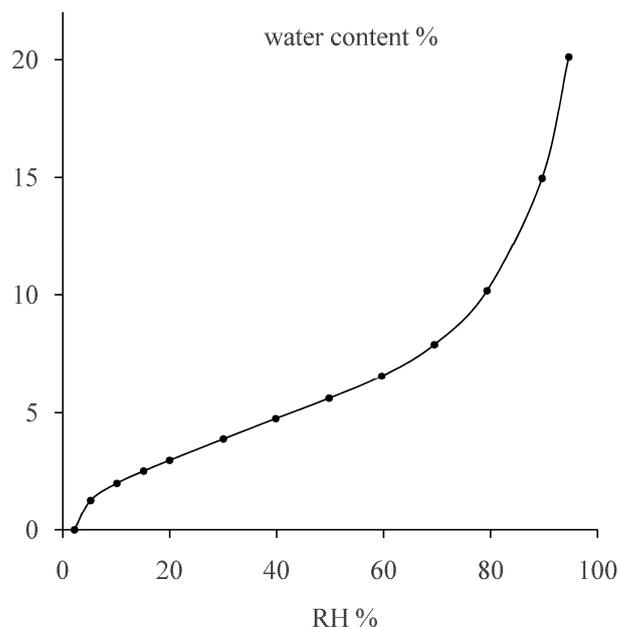


Fig. 3: Water absorption isotherm of pure cellulose paper

Early accelerated ageing experiments implemented arid ovens (TAPPI T 453). The atmosphere inside the oven was not controlled and the relative humidity (RH) was very low (less than 1%). Later, it was recognized that some moisture in the ageing environment was necessary for accelerated ageing to resemble natural ageing (Graminski et al., 1979; Wilson and Parks, 1983). The apparent effect of moist ageing was the speeding of the degradation rate (Browning and Wink, 1968; Roberson, 1976; Arney and Jacobs, 1979; Graminski et al., 1979; Wilson and Parks, 1979; Zou et al., 1994; Zou et al., 1996a). Investigation of the degradation products revealed though that changes in RH altered the degradation process, that is the relative contribution of the various reactions comprising what is

collectively called ageing, where changes in temperature at the same RH only changed the degradation rate (Erhardt and Mecklenburg, 1995; Shahani et al., 2001). It was concluded that at 30-80% RH, accelerated ageing results were within the range of natural ageing results, considering the variation of the conditions of natural ageing, while those of aging in arid ovens were not (Erhardt and Mecklenburg, 1995). An important breakthrough was the realization that it is not the RH but the moisture content of the paper that is important (Graminski et al., 1979; Zou et al., 1996a; Shahani et al., 2001). The moisture content of paper is defined by the RH and the temperature of the environment. The dependence on RH is not linear and is described by the water absorption isotherm (Fig. 3). Several authors observed the similarity of the water absorption isotherm to the plots of the degradation rate versus RH and assumed that the degradation rate depends on RH in a similar manner (Graminski et al., 1979; Zou et al., 1996a; Shahani et al., 2001). This observation suggests a roughly linear relationship between degradation rate and moisture content (Zou et al., 1996a) but is in contrast with Erhardt's results (Erhardt and Mecklenburg, 1995), which showed that an increase of RH from 30% to 50% does not double (as predicted from the isotherm) but triples to quintuples the degradation rate. It has been suggested that ageing under RH cycling conditions is at least as fast as that at the higher RH value, and that RH cycling may in fact enhance the degradation rate (Luner, 1969; Shahani et al., 1989)

Since the moisture content determines the degradation pathway, it was proposed that in order to better simulate natural ageing, accelerated ageing experiments should be performed in atmospheres that maintained the moisture content of paper at the same level as at the ambient conditions (Shahani et al., 2001). That, together with the need to retain the degradation products in the ageing atmosphere led to a shift in experimental setups from humid circulating ovens to sealed vessels with fixed moisture content. By preconditioning the contents of the vessels at controlled ambient conditions (23°C and 50%RH, TAPPI T 402), it was made possible to maintain about the same moisture content of paper at the temperature of ageing. This setup was used in some early studies (Browning and Wink, 1968), but it has been recently recommended in a newly adopted standard (Kaminska et al., 2001; Shahani et al., 2001; ASTM D 6819-02, 2002; Begin and Kaminska, 2002).

It is not surprising that moisture content greatly affects degradation, since water plays a manifold role in cellulose degradation (Strlič et al., 2005a). Water is an essential reactant in acid hydrolysis (Zou et al., 1996a) and numerous studies cited above highlight the acceleration of degradation with increasing moisture content. It also serves as a swelling agent, increasing thus the surface area available for reactions (Gregg, 1982) and acts as a plasticizer by promoting molecular mobility. Its polarity facilitates dissociations and there is evidence that reactions in paper occur in a similar manner as in aqueous solutions (Strlic et al., 2001).

Concerning the storage of paper in archives, libraries and museums, the recommended relative humidity lies between 25-60% (the BS 5454, 2000 recommends 45-60%, the AS 4390, 1996 45-55%), the lower RH preferred for paper collections alone (Erhardt and Mecklenburg, 1995) and the higher values for mixed collections including materials that cannot withstand low RH values.

4.3. pH

The pH of paper⁵ is considered the most important factor determining its stability towards natural and accelerated ageing (Barrow and Sproull, 1959; Roberson, 1981; Wilson and Parks, 1983). Numerous studies have shown that acidity accelerates the degradation of cellulose and paper via acid-catalyzed hydrolysis (Barrow and Sproull, 1959; Arney and Chapdelaine, 1981; Wilson and Parks, 1983, also see above). The importance of acidity has been demonstrated in the studies of naturally aged paper, which show that weak, discoloured and brittle paper correlates with low pH, while neutral and alkaline papers are generally in a much better preservation status (Barrow and Sproull, 1959; Barrett, 1989; Waterhouse and Barrett, 1991; Zyska, 1996; Sobucki and Drewniewska-Idziak, 2003). It has also been shown that deacidified paper degrades more slowly than before deacidification, the effect being more intense for highly acidic paper (Lienardy, 1991, 1994; Kolar and Novak, 1996; Sistach, 1996; Bansa, 1998; Bukovsky, 1999). As a result, standards for permanent paper were based mainly on paper's alkalinity (ISO 9706; ISO 11108; ANSI/NISO Z39.48) and the paper industry, acknowledging the fact that alkaline paper exhibits the high permanence required by end-users, shifted gradually during the last 30 years from acidic to alkaline paper production (Stuhrke, 1977; Hagemeyer, 1981; Sclawy and Williams, 1981; Crouse and Wimer, 1991; Zappala, 1991). However, as discussed above, under neutral or alkaline conditions the degradation of paper and cellulose does not entirely cease and the mechanism changes from acid-catalyzed hydrolysis to autoxidation.

⁵ Since paper is not a solution, pH cannot be rigorously defined for it. An arbitrary definition of pH for paper that serves as an indication of its acidity specifies that it equals the pH of the extract of a certain quantity of paper in a volume of water. The exact quantities of paper and water depend on the standard used, and for ISO 6588 (1981) are 2 g of paper in 100 ml of water.

Arney and Chapdelaine (1981) used the time-ratio technique (see below) for the study of the effect of acidity on the rate of ageing. They aged a newsprint and a rag paper at 90°C and 100% RH, in nitrogen and air atmospheres and calculated the rate of ageing from yellowing and tensile strength loss. The total rate of ageing was expressed as the sum of the atmospheric oxidation rate plus the oxygen independent oxidation rate. The rates of these two processes depended linearly on the hydrogen ion concentration. The dependence of the ratio of the rate of degradation in nitrogen over that in air on acidity is presented in the next equation:

$$i = \frac{k_{b1}[H^+] + k_{b2}}{k_{a1}[H^+] + k_{a2} + k_{b1}[H^+] + k_{b2}} \quad (1), \text{ where } k_{a1}, k_{a2}, k_{b1}, k_{b2} \text{ constants and the subscripts a and b}$$

referring to degradation in air and nitrogen respectively.

It was also concluded that the relative contribution of the two processes was independent of the pH at the range studied (4 - 9), suggesting that the same must be true for the natural ageing of paper (Arney and Novak, 1982).

The dependence of the rate of ageing on the moisture content and the pH of the cellulose samples was analyzed and quantified by Zou et al. (1996a). It was found that the pH and the moisture content affect only the frequency factor of the Arrhenius equation (see below) as shown in the next equation:

$$A = A_0 + A_1[H_2O] + A_2[H^+][H_2O] \quad (2), \text{ where } A \text{ is the apparent frequency factor of the complex system and } A_0, A_1 \text{ and } A_2 \text{ are constants. The linear dependence of the frequency factor on the hydrogen ion concentration and moisture content was verified experimentally for 3 bleached kraft pulps.}$$

4.4. OPEN VS CLOSED ENVIRONMENTS

In the early applications of accelerated ageing, arid circulating ovens were used. These ovens create an open environment, allowing for the escaping of the volatile degradation products. In an attempt to investigate the results of moist ageing, sealed tubes were used occasionally with preconditioned samples at ambient conditions (Browning and Wink, 1968). This setup ensures a strict control of the moisture content of paper in a convenient and inexpensive manner, considering that the other option is the use of expensive and failure-prone ageing chambers with relative humidity control. The effect of the trapped degradation products on the rate of ageing was not recognized at that time.

Shahani et al. (1989), when studying the result of RH cycling, measured higher degradation rates for samples arranged in stacks of 100 leaves instead of single leaves. It was assumed that the acceleration of the ageing process was due to the retention of the volatile acidic products of paper decomposition. In a later study, Shahani and Hengemihle (1995) proposed the use of sealed vessels with preset relative humidity (accomplished by acclimatizing the samples to the required RH before sealing the vessels), because they believed that this setup emulates natural ageing better than the use of circulating ovens. Under these experimental conditions, significantly higher degradation rates were determined, compared with the rates determined from identical samples hung in humid circulating ovens. The plots of folding endurance against time of ageing indicated a gradual acceleration of the rate and assumed the characteristic curvature of an autocatalytic process. The authors suggested that the volatile acidic products of paper degradation, which were retained in the sealed vessels, were absorbed by the paper samples and accelerated their ageing (autocatalysis). Deacidification of the samples prior to sealing or the inclusion of alkaline paper within the sealed vessels resulted in a significant drop of the degradation rate. Nevertheless, other researchers that adopted ageing in sealed vessels or stacks did not observe the aforementioned gradual acceleration

of the ageing rate (Zou et al., 1996a; Kaminska et al., 2001; Barański, 2002; Barański et al., 2004), or found mixed trends (Barański et al., 2000)

By examining 18 books that have aged naturally for more than 100 years, Brandis and Lyall (1997) found that a statistically significant part of them had the inner pages weaker than the outer ones. Although no sound experimental evidence that accounted for their observations was found, they stressed the relevance of their findings with the results of Shahani et al. (1989) and Shahani and Hengemihle (1989), who reported faster ageing for paper samples aged together with their degradation products (accelerated ageing in stacks or sealed vessels).

Shahani et al. (Shahani et al., 2001) studied extensively the ageing in sealed vessels and concluded that this mode of ageing better emulates natural ageing than single sheet ageing in circulating ovens. Their results, together with those of other researchers, verified that natural and accelerated ageing produce volatile acidic substances (see above) that are absorbed from the paper matrix and gradually accelerate the rate of ageing and consolidated the autocatalysis hypothesis. On the basis of their findings, they proposed a new standard which adopted ageing in sealed vessels (ASTM D 6819-02, 2002). Zervos and Moropoulou (2005) and Zervos (2007a) aged pure cellulose paper for long periods (up to 240 days) in sealed vessels and found that the acceleration of the degradation rate reflected on all properties studied. They proposed a kinetic model that accounted for the acceleration of the rate based on autocatalysis that applies to ageing in sealed vessels.

4.5. LIGHT

Light plays an important role in the natural ageing of paper. Light exposure sets off the production of free radicals, thus initiating the photooxidation of cellulose, which proceeds via a mechanism similar to cellulose autoxidation (Bos, 1972; Hon, 1975a, b, c, d, 1976; Andrady et al., 1991; Whitmore and Bogaard, 1995; Havermans and Dufour, 1997; Kolar et al., 2005). Photooxidation reduces the degree of polymerization and the strength of paper and cellulose, deteriorates their optical properties, especially those of lignin containing paper and introduces carbonyls and carboxyls on the cellulose backbone (Padfield, 1965; Hon, 1981; Kelly and Williams, 1981; Lee and Feller, 1986; Lee et al., 1989; Yang, 1991; Whitmore and Bogaard, 1994; Heitner, 1996; Bukovsky, 1997; Atalla et al., 2000; Bukovsky, 2000a, b; Bukovsky and Kuka, 2001; Dufour and Havermans, 2001; Bukovsky and Trnkova, 2003). Light exposure can also cause bleaching to paper, presumably because it oxidizes the chromophores produced by lignin degradation, or for non-lignin containing paper, converting the carbonyls to carboxyls (Bos, 1972; Hon, 1981; Lienardy and Van Damme, 1988; Lee et al., 1989; Heitner, 1996; Schaeffer et al., 1997; Atalla et al., 2000; Bukovsky, 2000a, b).

Pure cellulose does not absorb visible light (over 400 nm). It strongly absorbs UV light (under 200 nm), while in the intermediate region there is a weak absorption band with a peak at about 260 nm. This absorption maximum is attributed to the carbonyl groups (acetals or ketones, Bos, 1972; Hon, 1975a; Hon, 1981), which are considered to act as initiators of the photochemical reaction (Hon, 1975a). Hemicelluloses have similar behavior to cellulose, while natural and modified lignin strongly absorb in the UV and the visible region (Hon, 1981; Gellerstedt, 1996; Heitner, 1996). The problem of the colour instability of paper during ageing is well known to paper industry, where the development of yellowing is known by the term “colour or brightness reversion” (Hon, 1981; Heitner, 1996). The colour reversion in mechanical pulps is caused by the photooxidation of lignin. It is believed that the free phenolic radicals are involved, which are the precursors of the o-quinones, the later being the main responsible for the development of yellowing (Heitner, 1996).

The effect of light on paper has been reviewed by several authors (Padfield, 1965; Havermans and Dufour, 1997). Three mechanisms are reported: direct photolysis from UV light, photosensitized degradation from visible and near infrared and photochemical production of free radicals (Havermans and Dufour, 1997).

Bos (1972), after irradiating cellulose with UV light of 253.7 nm, reported yellowing and an increase of ketonic carbonyls for irradiation in vacuo, while in dry air he reported bleaching and production of carboxyl groups. Hon (1975a) studied the production of free radicals by electron spin resonance. He found that for wavelengths higher than 330 nm, no radicals were detected. Wavelengths between 280 and 330 nm produced H atoms, while lower wavelengths than 280 nm produced H atoms and formyl radicals (*CH=O). Hon also studied the effect of photosensitizers (Hon, 1975b) and concluded that lignin exerts a protective action on cellulose against photoirradiation (Hon, 1975c). The same opinion about the protective effect of lignin has been expressed by other authors (Gurnagul et al., 1993; Zou et al., 1993; Schmidt et al., 1995; Begin et al., 1998). Hon also attempted to identify the produced radicals (Hon, 1975d). A recapitulation of his research is presented in a next article (Hon, 1976). Lee and Feller (1986) impregnated filter paper with hemicelluloses and subjected it to photochemical and thermal ageing. Their results indicate that while thermal ageing induced intense discoloration, the results of light exposure were practically negligible. Moderate immediate depolymerization of cellulose and sensitization to subsequent thermal ageing was reported by Lee et al. (1989) when they subjected lignin-free paper to photochemical ageing. The authors suggested that photochemical ageing is a considerable degradation path for archival and library material if stored paper is exposed to light. The study of cotton cellulose photooxidation by means of FTIR photoacoustic spectroscopy (FTIR-PAS) revealed the production of carboxylic acids (Yang, 1991). Leclerc and Flieder (1992) studied the effect of the optical brighteners (stilbene derivatives) on the stability of paper towards light and concluded that their use should better be avoided in papers made of pure cellulose. The photooxidation of groundwood paper was examined by Bukovsky (1997), who found a direct correlation between lignin content and oxidation (expressed as carbonyl content) and yellowing. No correlation was found between photooxidation and pH, but the better behavior of deacidified samples was attributed to the ability of the alkaline earth metals to neutralize the peroxide radicals. The effects of deacidification on the resistance of paper towards photochemical ageing has also been discussed in a number of studies (Bukovsky, 2000a, b; Bukovsky and Kuka, 2001; Dufour and Havermans, 2001; Bukovsky and Trnkova, 2003). Atalla et al. (2000) reported that visible light plays a more significant role than ultraviolet radiation in the photo-yellowing of lignin free papers when they are were exposed for extended periods of time. They also reported that lignin containing papers that were susceptible to direct photochemical reactions were also susceptible to photo-initiated dark reactions, which had a marked effect on the darkening of the samples. According to their results, the calcium carbonate-containing papers were brighter both before and after light exposure. Acidic papers were found to be more susceptible to darkening, but the crucial factor affecting photoyellowing is the lignin content (Forsskåhl, 2000). Experimental results indicate that the mechanisms for aging with pollutants, light and heat are all different from each other and are also fiber dependent (Forsskåhl, 2000).

4.6. POLLUTION

Paper stored in atmospherically polluted areas may exhibit increased acidity because of the absorption of acidic pollutants (Hudson, 1967a; Baer and Berman, 1986). Such pollutants are the sulphur dioxide (SO₂) and the nitrogen oxides (NO_x), which are absorbed by paper and by oxidation and in the presence of moisture are converted to strong acids (Hudson and Milner, 1961; Hudson et

al., 1964; Hudson, 1967b; Edwards et al., 1968; Johansson et al., 2000). Apart from their activity as acids, they are strong oxidizing agents and together with ozone (O_3), other volatile organic compounds (VOCs) and particles suspended in the atmosphere can participate in a multitude of detrimental to paper longevity reactions. It has been suggested that NO_x and O_3 act as catalysts and/or oxidizing agents in the transformation of SO_2 to SO_3 (Johansson et al., 2000).

Daniel et al. (1990) studied the effect of a mixture of SO_2 (13ppm) and NO_2 (4ppm) for up to 12 weeks on three kinds of paper (made of cotton, chemical and mechanical pulp) which have been deacidified. They found that the ageing resistance of the filter and the newsprint paper was improved, but that of the chemical pulp paper deteriorated. Havermans (1995) reported on an extensive research of the results of pollution on various kinds of paper and of the effectiveness of 3 methods of mass deacidification for protecting paper from the action of pollutants (SO_2 , NO_2). His results indicate that SO_2 does not react with pure cellulose in the absence of other pollutants. The SO_2 pick-up depends on the concentration of additives and fillers in the paper, increases with increased RH and is generally proportional to the SO_2 concentration in the ambient atmosphere. Alkaline fillers and lignin increase the SO_2 absorption. There is a synergistic effect of NO_2 and high RH concerning the SO_2 absorption: When NO_2 is present, it is not absorbed by cellulose but enhances the effectiveness and the absorption of SO_2 . Thermal ageing of the artificially polluted paper resulted in a marked increase of the degradation rate. Deacidified and alkaline paper deteriorated more slowly than the acidic papers. Daniel (1996) describes a pollution chamber for the study of the effects of SO_2 and NO_2 on paper. A research project of air purification in the storage area of the Dutch State Archives is presented by De Feber et al. (1998).

The influence of the atmospheric pollutants on the longevity of various kinds of paper and the effect of lignin were studied by Begin et al. (1999). It was found that lignin and alkaline fillers increased the absorption of SO_2 and NO_x , but alkaline fillers significantly enhanced the resistance against pollution. The presence of lignin affected only the deterioration of optical properties. There was no correlation between the quantity of the absorbed pollutants and paper degradation. NO_x was found to affect more severely the optical properties. Johansson et al. (2000) studied the pollutant uptake by various kinds of paper and concluded that high RH and the presence of NO_x and O_3 enhance the absorption of SO_2 . The influence of SO_2 and O_3 on paper made of bleached chemical pulp was studied by diffuse reflectance FTIR spectroscopy (DRIFT) and time-resolved trace gas analysis by Johansson and Lennholm (2000). It was concluded that the protonation of the carboxylic groups is the initial step of their reaction with cellulose. Contrary to previously published results, Reilly et al. (2000) reported that the most virulent pollutant is NO_2 . NO_2 by itself caused more folding endurance loss and more yellowness from any other combination of the other pollutants.

4.7. OTHER FACTORS

Many other factors contribute to or modify the ageing process. The effect of the supramolecular structure of cellulose is discussed below in more detail, but here it is sufficient to say that degradation affects first the amorphous areas and slows down when the attack reaches the crystalline regions. Thus, the rate of degradation changes during the reaction according to the accessibility of the remaining cellulose chains. In addition, cellulose with high crystallinity index is degraded more difficultly and at lower rates. Supramolecular structure differences partially account for the differences in susceptibility to degradation observed between cotton and wood cellulose. The origin of cellulose and the processing of the raw material (degree of polymerization of cellulose, lignin and hemicelluloses content, metal contamination and high content of oxidized cellulose resulting from bleaching, degree of beating, additives and pulping system) affect the

degradation resistance. The role of lignin is somehow ambiguous; oxidized cellulose is unstable; transition metal ions catalyze the oxidation of cellulose; the increased acidity, usually the result of addition of alum, catalyzes the acid hydrolysis of cellulose; mechanical pulps are generally considered less stable compared to chemical pulps; these matters have been addressed in detail elsewhere in this review. The storage conditions are critical and determine the longevity of paper. Low temperature and low to moderate relative humidity maintain the degradation rate due to chemical reactions to acceptable levels. They also keep the population of biological agents (fungi, bacteria and pests) under control. Light exposure should be kept to a minimum and pollutants should be excluded from the atmosphere of the repositories.

5. CHANGES IN PAPER AND CELLULOSE PROPERTIES

Ageing causes an overall deterioration of the useful properties of paper and cellulose (Wilson et al., 1955; Wilson and Parks, 1979; Wilson and Parks, 1980; Wilson and Parks, 1983; Feller et al., 1986; Fellers et al., 1989). The most important chemical index of degradation, the degree of polymerization, decreases and the percentage of the cleaved bonds and the number of scissions increase because of acid-catalyzed hydrolysis with or without chain scission induced by oxidation or light exposure. The pH decreases because of the production of acidic species. The copper and the kappa number (ISO 302; TAPPI T 430), both indicators of oxidizable content generally increase, together with the content of carbonyls and carboxyls. Alkali solubility, a general indicator of degradation, increases also.

The decrease of the degree of polymerization straightforwardly affects all the mechanical properties. Folding endurance (FE) is the first strength property to be affected. The great sensitivity of FE in detecting the effects of ageing is regrettably counterbalanced by the low repeatability of its determination (Browning and Wink, 1968; Browning, 1977; Fellers et al., 1989; Shahani, 1995; Shahani et al., 2001; Zervos and Moropoulou, 2006; Zervos, 2007c). Stretch at break and tensile energy absorption, together with tearing resistance are less sensitive to degradation than FE, but more sensitive than tensile strength (TS). It has been reported that even severely naturally or artificially aged paper retains a large proportion of tensile strength (Brandis, 1994; Bansa and Ishi, 1997, 1999; Zervos and Moropoulou, 2006; Zervos, 2007c). There are contradicting reports concerning the effect of ageing on the Young's modulus (or elastic modulus, or extensional stiffness). Graminski (1970) found an increase of the Young's modulus and the wet strength, which he attributed to either the crosslinking of the cellulose chains or the increase of crystallinity. Considering that similar changes occur in natural ageing, he took these similarities as an indication that accelerated and natural ageing involve similar processes. On the other hand, Zou et al. (Zou et al., 1994) found that the elastic modulus was not affected by ageing and attributed the difference between his results and those of Graminski to the effects of lignin and hemicelluloses. On the same matter, Erhardt et al. (1999) reported minimal differences in elastic modulus. The effect of ageing on wet strength is somehow ambiguous, and depends on the extent of crosslinking. If crosslinking occurs to an extensive degree, the results of crosslinking may overcome those of chain scission and the wet strength may increase considerably (see above). Bonding area and bond strength are not affected by ageing (Zou et al., 1994).

The optical properties of paper and cellulose are also affected by ageing (Lewin, 1965; Wilson and Parks, 1979, 1983; Berndt, 1989; Fellers et al., 1989; Andrady et al., 1991; Heitner, 1996; Atalla et al., 2000; Forsskåhl, 2000; Zervos and Moropoulou, 2006; Zervos, 2007c). The brightness (B), the lightness (L^*) of the CIEL*a*b* color system and the whiteness (W) decline, while the yellowness and the b^* (shift to yellow) and a^* (shift to red) coordinates of the CIEL*a*b*

color system increase (TAPPI T 524; TAPPI T 525; TAPPI T 452; ASTM D 2244-93; Malacara, 2002).

Various other properties are influenced by ageing. The water absorption and the water retention value of paper and cellulose drop with ageing (Kato and Cameron, 1999a, b). Ageing, either natural or artificial promotes hornification, which is defined as the irreversible changes in water sorption behaviour that result from water removal, either at ambient or elevated temperature, with lower flexibility, lower water retention and increased brittleness being its main characteristics (Kato and Cameron, 1999a). It is attributed to the formation of irreversible intra-fibre hydrogen bonding between microfibrils. It has been reported that the porosity of pure cellulose paper decreases after ageing and there are indications that the larger pores are affected more (Zervos, 2007b). It has been speculated that the ageing of cellulose should have an impact on the degree of crystallinity. The high temperature used for ageing and the absorbed moisture are supposed to promote the mobility of cellulose chains, which having suffered cleavage due to degradation are much easier to aggregate in a more ordered fashion than when intact (Atalla, 1981). Measurements of crystallinity before and after ageing failed to prove beyond doubt that crystallinity increases, since some results indicated no measurable changes (Major, 1958; Moharram et al., 1981; Kato and Cameron, 1999b) while others indicated a small increase (Atalla, 1981; Zervos, 2007b).

Several publications discuss which properties of cellulose and paper are the most useful for detecting changes caused by ageing and for the monitoring of the ageing process. Wilson and Parks (1979; 1983) discussed the ageing process, the possible reactions involved and the effects of ageing on the paper properties. For finding what happens during ageing, they propose the following tests: zero span tensile strength (fibre strength), the ratio of the wet over the dry tensile strength (crosslinking), pH (acid formation), alkali solubility (depolymerization), functional group content (oxidation, hydrolysis) and molecular chain length distribution (depolymerization, randomness of position). They also suggest the following tests for detecting changes during the ageing: folding endurance, tear resistance, stretch at break, tensile energy absorption, alkali solubility, copper number and viscosity. Shahani et al. (2001) recommend the use of M.I.T. folding endurance and the tear strength tests before and after ageing in sealed tubes for the evaluation of permanence (ASTM D 6819-02). Others propose the determination of the DP, the folding endurance, the colour coordinate b^* of CIELAB and the cold extraction pH together with ageing tests in sealed vessels as the most sensitive and meaningful tests for the evaluation of paper conservation interventions (Zervos and Moropoulou, 2006; Zervos, 2007c).

The kinetics of the property change vary according to the property and the environment of ageing. Several important properties or suitable transformations of them (FE, percentage of the cleaved bonds, number of scissions, inverse DP, intrinsic fluidity, tensile strength and brightness) often exhibit a linear relationship with the ageing time in open environments (circulating ovens, see below), while in closed environments they assume accelerating shapes, indicating autocatalytic processes in action (Shahani, 1995; Shahani et al., 2001; Zervos and Moropoulou, 2005).

The natural ageing of cellulose presents some unique phenotypes, associated with special degradation paths. Foxing, that is the staining of paper with circular rust-coloured stains is associated with either microbial activity (Meynell, 1979; Gallo and Hey, 1988; Florian, 1996; Florian and Manning, 1999) or oxidative degradation due to high concentration of transition metal ions (Ligterink et al., 1991; Choisy et al., 1997; Rebrikova and Manturovskaya, 2000; Bicchieri et al., 2001). Iron gall-ink corrosion is the degradation of paper caused by the corrosive iron-gall ink (Van Gulik and Kersten-Pampiglione, 1994; Neevel, 1995; Banik, 1997; De Bruin, 1997; Metz, 1997; Sellink, 1997; Van der Windt, 1997; Van Gulik, 1997; De Feber et al., 2000; Budnar et al.,

2001; Kolar and Strlic, 2004; Kolar et al., 2007; Potthast et al., 2008). In the early stages it causes the appearance of the writing in the opposite side of the leaf. In an advanced state it causes embrittlement and crumbling of the paper in the vicinity of the writing. Dark lines are often found in old paper. They are usually caused by water staining and have been associated with the oxidation of cellulose (Dupont, 1996a; Dupont, 1996b). The various phenotypes of discoloration and their causes are reviewed by Daniels (1988).

6. KINETIC STUDIES OF PAPER AND CELLULOSE AGEING

There are two distinct stages with different objectives in the kinetic study of a chemical reaction (Arney and Chapdelaine, 1981). In the first stage, the determination of the order and the rate constant k of the reaction is pursued. In this stage, the concentrations of a reactant or of a product of the reaction are followed during the evolution of the reaction. In the second stage, the activation energy E_a and the pre-exponential (or frequency) factor A of the reaction are determined by applying the Arrhenius equation:

$$k = A e^{-\frac{E_a}{RT}} \quad (3) \quad \text{or} \quad \ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A \quad (4)$$

where k is the reaction rate, R the gas constant (8.314 J/mol·K) and T the absolute temperature.

In the case of paper and cellulose ageing, the determination of the concentration of the reactants or of the products of the reaction is not feasible, since they both consist of cellulose molecules of various lengths. The determination of the rate constant k is achieved by following either a function of the DP of cellulose (usually the inverse DP) or a physical property (folding endurance or brightness) of the paper samples. The second approach is empirical and was applied in the early studies of paper and cellulose ageing kinetics. Contrariwise, the inverse DP (or the percentage of the cleaved glycosidic bonds which is proportional to inverse DP) represents true kinetic data since it has been derived by using kinetic principles (Zou et al., 1996a, b).

6.1. KINETIC STUDIES BASED ON DP - KINETIC MODELS

It has been generally assumed that the degradation of cellulose follows a first order reaction, which can be approximated in the early stages by a zero order reaction.

Let: c = total number of cellulose molecules, DP = number-average Degree of Polymerization, g = total number of glucose molecules and N = total number of glycosidic bonds.

Then: $DP - 1$ = average number of glycosidic bonds per cellulose molecule, $N = c(DP - 1)$ = total number of glycosidic bonds, $c DP = g$ = total number of glucose molecules and

$$c = \frac{g}{DP} \Leftrightarrow c(DP - 1) = \frac{g}{DP}(DP - 1) \Leftrightarrow N = g\left(1 - \frac{1}{DP}\right) \quad (5)$$

Assuming a first order reaction, the rate of bond cleavage is proportional to the bond concentration:

$$\frac{d[N]}{dt} = -k[N] \quad (6), \quad \text{where } t \text{ is the time and } k \text{ the rate constant}$$

$$(6) \Rightarrow \ln N_0 - \ln N_t = k t \quad (7), \quad \text{where } N_0 \text{ and } N_t \text{ the number of bonds at times } 0 \text{ and } t.$$

$$(5), (7) \Rightarrow \ln\left[g\left(1 - \frac{1}{DP_0}\right)\right] - \ln\left[g\left(1 - \frac{1}{DP_t}\right)\right] = kt \Rightarrow$$

$$\ln\left(1 - \frac{1}{DP_0}\right) - \ln\left(1 - \frac{1}{DP_t}\right) = kt \quad (8), \text{ kinetic law based on first order reaction}$$

For high values of DP, eq. (8) can be simplified to:

$$\frac{1}{DP_t} - \frac{1}{DP_0} = kt \quad (9), \text{ kinetic law approximation, pseudo zero order reaction}$$

Equation (9), which is the approximation of the first order kinetics (pseudo zero order) and applies to the early stage of the reaction, can be derived by directly assuming that in the beginning of the reaction the number of bonds N in eq. (6) remains practically constant ($k[N] \approx \text{constant} = \kappa$). Under this condition, equation (6) becomes eq. (10), which describes a zero order reaction.

Assuming a zero order reaction, the rate of bond cleavage is constant:

$$\frac{d[N]}{dt} = -\kappa \quad (10), \text{ where } t \text{ is the time and } \kappa \text{ the rate constant}$$

$$(10) \Rightarrow N_0 - N_t = \kappa t \quad (11), \text{ where } N_0 \text{ and } N_t \text{ the number of bonds at times } 0 \text{ and } t.$$

$$(5), (11) \Rightarrow g\left(1 - \frac{1}{DP_0}\right) - g\left(1 - \frac{1}{DP_t}\right) = \kappa t \text{ and by setting } k' = \kappa/g,$$

$$\frac{1}{DP_t} - \frac{1}{DP_0} = k' t \quad (9a), \text{ kinetic law based on zero order reaction}$$

Regardless of the reaction order, the percentage of the cleaved glycosidic bonds in time t can be calculated from the values of DP_t and DP_0 (Zervos and Moropoulou, 2005):

$$cDP = g \Rightarrow \frac{1}{DP} = \frac{c}{g} \text{ and}$$

$$100 \left(\frac{1}{DP_t} - \frac{1}{DP_0} \right) = 100 \left(\frac{c_t}{g} - \frac{c_0}{g} \right) = 100 \frac{(\text{number of new cellulose molecules})}{g} =$$

$$100 \frac{(\text{number of cleaved bonds})}{g} = 100 \frac{(\text{number of cleaved bonds})}{N_0},$$

$$\text{since for large } DP_0, \frac{1}{N_0} = \frac{1}{c_0(DP_0 - 1)} \approx \frac{1}{c_0 DP_0} = \frac{1}{g}$$

$$\text{Therefore, \% cleaved bonds} = \delta\% = 100 \left(\frac{1}{DP_t} - \frac{1}{DP_0} \right) \quad (12)$$

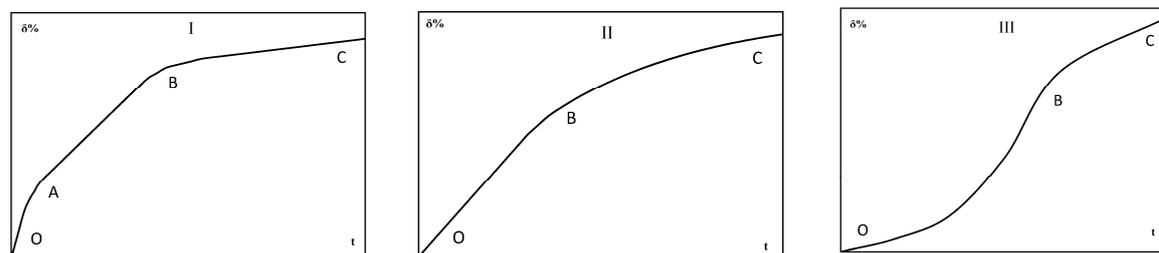
By combining equations (9) with equation (12), the following equation is obtained, which applies regardless of the reaction order for the early stages of degradation:

$$\delta\% = K t \quad (13), K = 100k, \text{ kinetic law, early stages of degradation}$$

According to equations (9) and (13), the dependence of $\delta\%$, of the inverse DP (often found in the literature as “fluidity”) or of the difference of the inverse DP on time at the early stages of

degradation is linear, allowing for the determination of the rate constant k from the slope of the plot by linear regression.

The first order model and the derivative equations (8) and (9) were introduced by Ekenstam (1936) and have been used since together with eq. (13) and other variations of them for the monitoring of cellulose degradation (Krassig and Kitchen, 1961; Michie et al., 1961; Fung, 1969; Shafizadeh and Bradbury, 1979; Marx-Figini and Coun-Matus, 1981; Feller et al., 1986; Fellers et al., 1989; Lee et al., 1989; Emsley and Stevens, 1994; Zou et al., 1994; Hill et al., 1995a; Zou et al., 1996a; Kolar et al., 2005; Gilbert et al., 2008), regardless of the mechanism of the reaction. Zou et al. (1996a) derived equation (9) without any initial assumption concerning the order of the reaction and Hill et al. (1995a) by using the zero order approach. Shafizadeh and Bradbury (1979) and Feller et al. (1986) showed that both first order and zero order can lead to equation (9) and suggested (Feller et al., 1986) that conformance to it should not be taken as proof of first order kinetic behavior. The kinetic models presented above were developed for monitoring the acid hydrolysis of cellulose, a reaction taking place in a solution, but have been found to apply also to the heterogeneous reactions of thermal (including thermal accelerated ageing), photochemical and enzymatic degradation of cellulose (Shafizadeh and Bradbury, 1979; Feller et al., 1986; Kolar et al., 2005). The applicability of equation (9) is so wide, that it has been found to apply even to the thermal ageing of kraft paper in oil (Emsley and Stevens, 1994; Hill et al., 1995a; Gilbert et al., 2008). The temperature range of the applicability of these models starts from ambient temperatures and reaches at least up to 200°C, surpassing by far the higher limit of the temperatures applied for accelerated ageing (Fung, 1969; Shafizadeh and Bradbury, 1979; Emsley and Stevens, 1994; Hill et al., 1995a).



I. The three-stage scheme suggested by Feller et al. (1986). OA: Initial rapid stage, hydrolysis of the weak links. AB: Steady-rate stage, hydrolysis of the bonds in the amorphous regions. BC: Final slow stage, attack on the crystallites. B: $\delta\%$ corresponding to LODP.

II. The most commonly reported scheme of cellulose degradation. Similar to (I) but with the first stage of the weak-links hydrolysis missing.

III. Degradation of cellulose in sealed vessels (Zervos and Moropoulou 2005; Calvini et al. 2007, 2008). OB: Autocatalysis domain. BC: Attack on the crystallites. B: $\delta\%$ corresponding to LODP (reported values of $\delta\%$ around 0.6-07%)

Fig. 4: Stages of cellulose degradation. Plots of the percentage of the cleaved bonds ($\delta\%$) against ageing time.

Nevertheless, certain requirements must be met for the application of equation (9): the polymer must be linear and monodisperse, the initial DP must be high, the scission must be random and the reaction must be in the initial stage (Emsley and Stevens, 1994). There seems to be a degree of arbitrariness in this last requirement, but its quantification depends on the origin and properties of the specific sample of cellulose. It has been reported that heterogeneous cellulose degradation can be regarded as taking place in two or three stages (Fig. 4) (Feller et al., 1986). In the first rapid stage, the so called “weak links” or “acid sensitive links” are hydrolyzed. It has been suggested that there are 18-28 such links for every 10000 normal bonds (Michie et al., 1961; Daruwalla and Narsian, 1966; Marx-Figini and Coun-Matus, 1981) that react up to 10^4 times (Feller et al. 1986) or 3 to 4 times (Rånby, 1961) faster than the normal bonds. Their sensitivity has been attributed to either the mechanical stresses because of the folding of the cellulose chain (Sharples, 1954b, a;

Michie et al., 1961; Emsley and Stevens, 1994), or to the oxidized groups of the glucopyranose ring (carbonyls and carboxyls, Rånby, 1961) which destabilize the neighboring glycosidic bonds due to their inductive effect and cause beta-alkoxy-elimination (Golova and Nosova, 1973; Feller et al., 1986; Bicchieri and Pepa, 1996; Whitmore and Bogaard, 1995; Dupont, 1996a; Margutti et al., 2001). This first stage has been rather rarely reported (Schultz, 1948; Michie et al., 1961; Rånby, 1961; Shafizadeh and Bradbury, 1979). In most of the relevant studies, the degradation of cellulose starts with a steady rate stage, which follows equation (9) and which is the second stage in the classification of Feller et al. (1986). In this stage, the bonds in the amorphous part of cellulose are hydrolyzed at random positions. At the end of the steady rate stage, a deceleration of the reaction has been universally reported (in heterogeneous conditions) by researchers that followed degradation for long ageing times, marking the beginning of the slow final stage, the attack to the crystalline regions. At this point, the applicability of equation (9) ends. The deceleration of the reaction starts when the DP of cellulose reaches a value called Limiting Value of the Degree of Polymerization (LODP), which is assumed to be the value of the DP of cellulose crystallites and which depends on the origin and the processing of the cellulose sample. Values of LODP ranging from 400 to 200 have been reported (Krassig and Kitchen, 1961; Shafizadeh and Bradbury, 1979; Feller et al., 1986; Emsley and Stevens, 1994; Emsley et al., 1997; Klemm et al., 1998). Zervos and Moropoulou (2005) reported a value of DP around 250 and of cleaved bonds % ($\delta\%$) around 0.6-0.7 at the starting point of the deceleration of the reaction rate. The same value of cleaved bonds marking the onset of the third stage of cellulose degradation was also reported by Feller et al. (1986). It should be noted that around the end of the second stage, the useful strength of cellulose and paper has been lost (Feller et al., 1986; Zervos and Moropoulou, 2005). Feller's three stage classification is a useful tool for analyzing the degradation course but as the scientist states is a simplification of the effect of the various degrees of accessibility of cellulose to the degradation rate.

Zou et al. (1996a) showed that regardless of the reaction order, the full differential equation for cellulose degradation reads:

$$\frac{dDP}{dt} = -k(t)DP_o^2 \quad (14), \text{ where } k(t) = \lim_{\Delta t \rightarrow 0} \frac{m(t)}{N\Delta t} \quad (15)$$

the relative rate of bond breakage, $m(t)$ the bonds broken in time Δt and N the total number of glucose units. Assuming that the bond breakage rate $k(t)$ is constant, the classic kinetic equation (9) is obtained.

A different kinetic model based on the general differential equation proposed by Zou et al. (1996a) but taking into account the effect of crystallinity on the reaction rate has been proposed by Emsley et al. (1997) and Heywood et al. (1999). This model interprets the experimental results for long degradation times (second and third stage of cellulose degradation) in a uniform fashion. By assuming that the bond breakage rate of Zou et al. (1996a) (eq. 15) decreases by a typical first order process, $k(t) \equiv k_1 = k_1_0 e^{-k_2 t}$, equation (16) is obtained:

$$\frac{1}{DP_t} - \frac{1}{DP_o} = \frac{k_1_0}{k_2} (1 - e^{-k_2 t}) \quad (16), \text{ where: } k_1_0 \text{ and } k_2 \text{ are constants.}$$

They also propose an equation describing the change in tensile strength.

Calvini (2005) suggests that in order to follow the heterogeneous hydrolysis of cellulose (as is the case in degradation during accelerated ageing) the influence of the LODP should be taken into account. He introduces a modification of equation (8) which is equivalent to the Emsley model (1997) but with a physical meaning of the pre-exponential factor (dependence on the LODP):

$S = n^o(1 - e^{-kt})$ (17), where $S = \left(\frac{1}{DP_t} - \frac{1}{DP_o}\right)$: number of scissions per anhydroglucose unit,

$n^o = \frac{1}{LODP} - \frac{1}{DP_o}$: initial amount of cellulose bonds per anhydroglucose unit and LODP: the

Limiting Value of the Degree of Polymerization.

He also suggests that in order to correct the kinetic model for the deviations caused by the existence of weak links, the presence of two simultaneously occurring reactions should be considered:

$S = n_w^o(1 - e^{-k_w t}) + n_a^o(1 - e^{-k_a t})$ (18), the subscripts w and a refer to the weak and the amorphous links respectively.

The application of eq. (18) to previously published experimental data of cellulose hydrolysis in HCl at 60°C (Soubelet et al., 1989) gave a better fit than that of a single first order kinetics.

Calvini and Gorassini (2006), in a subsequent paper give an alternative definition to S , suggesting that a ratio between the values of DP can minimize the sources of errors resulting from DP determinations, which are exaggerated by the previous definition:

$$S = \frac{DP_o}{DP_t} - 1 \quad (19)$$

By applying the new definition of S , eq. (17) becomes:

$$\frac{DP_o}{DP_t} - 1 = \left(\frac{DP_o}{LODP} - 1\right)(1 - e^{-kt}) \quad (20)$$

He also suggests that accelerated ageing experiments should last at least until the LODP has been reached, unless they can be misleading.

The influence of the sealed environment on the degradation kinetics of cellulose has been studied by Zervos and Moropoulou (2005). Sealed vessels containing saturated solutions of NaCl for the adjustment of the relative humidity at 76±1% were used for the ageing of the samples at 80°C for up to 150 and 240 days. It was verified that the acidic degradation products of paper ageing caused an acceleration of the degradation reaction. A kinetic model based on autocatalysis (eq. 21) was derived theoretically by assuming that the production of acids is governed by first order kinetics. The testing of the model against the experimental data resulted in very good fittings.

$\delta\% = a(2^{kt} - 1)$ (21), where $\delta\%$ the percentage of the cleaved bonds and a and k constants

Similar equations were proposed for several physicommechanical properties of pure cellulose paper:

$P = P_o \pm C(2^{k_p t} - 1)$ (22), where P and P_o the property values at times t and 0, C and k_p constants.

The properties that were tested and found to conform to eq. (22) are: folding endurance, tensile strength, tensile energy absorption, stretch at break and the L^* and b^* coordinates of the CIEL*a*b* color system. The model applies until $\delta\%$ reaches 0.6-0.7% with a corresponding DP of around 250, which is in the range of reported LODP values (Krassig and Kitchen, 1961; Shafizadeh and Bradbury, 1979; Feller et al., 1986). After that the degradation decelerates (Fig. 4, III). At that point the folding endurance of the paper samples had dropped to zero, the tensile energy absorption to the 1/6 and the tensile strength to about the 2/3 of their original values. In a subsequent paper, Zervos (2007a) verified that eq. (21) and (22) also applied to pure cellulose paper treated with standard conservation procedures (washed, alkalized and strengthened with methylcellulose).

Calvini et al. (2007) proposed a system of equations representing a kinetic model of autocatalytic degradation applicable for ageing in sealed vessels. The qualitative study of the system indicated that the more important factor affecting the shape of the kinetic plot is the initial pH. Low initial acidity resulted in S-shaped kinetic plots.

Ding and Wang (2005; 2007; 2008b) introduced a new variable for the study of cellulose degradation called “accumulated DP loss” and defined as: $\omega_{DP} = 1 - \frac{DP}{DP_0}$ (23).

They also developed a new model equation based on accumulated DP loss describing the degradation of cellulose:

$\omega_{DP} = \omega_{DP}^* (1 - e^{-k_{DP}t})$ (24), where ω_{DP}^* is defined as the capacity of the DP degradation reservoir and k_{DP} the reaction rate constant. The application of eq. (24) to previously published data (even to cases of autocatalysis) resulted in better fittings than the application of other existing kinetic models.

The same researchers (Ding and Wang, 2008b) introduced an analogous equation to eq. (24) modeling the loss of tensile strength:

$\omega_{TS} = 1 - \frac{TS}{TS_0} = \omega_{TS}^* (1 - e^{-k_{TS}t})$ (25), where ω_{TS}^* is defined as the capacity of the TS degradation reservoir and k_{TS} the TS degradation rate constant.

The model of Ding and Wang (2008b) has been criticized by Calvini (2008) on the ground that the variable ω_{DP} is a “badly selected unit of measure”, since in Calvini’s opinion it introduces unnecessary complication and obscures the information in the kinetic plots. He also claims that the kinetic equation of Ding and Wang may lead to negative values of DP and tensile strength. Respectively, Ding and Wang (2008a) criticized Calvini’s model and defended theirs by presenting evidence that his model does not work in cases where their model gives very good fits of the experimental data. They also claim that Calvini’s degradation variable, as defined by eq. (19) does not apply for the characterization of the chain scission activity of cellulose.

Elaborating further on a general kinetic model that takes into account any possible variation of initial conditions and degradation environment, Calvini et al. (2008) introduce a system of equations which owing to its non-linearity does not allow for an analytical solution but can be analyzed by means of a two-stage model. The model is characterized by an autoretardant and an autocatalytic branch, the first applicable to the acid-catalyzed hydrolysis of cellulose (large excess of acid, $dH/dt \approx 0$) or for ageing in ventilated ovens (acidic products of degradation being removed, $dH/dt = 0$) and the second to aging in sealed vessels (autocatalysis). The hydrolytic degradation is considered to be the sum of three simultaneous hydrolytic reactions of the weak bonds and of the bonds in the amorphous and the crystalline regions, the kinetic equation being analogous to eq. (18) plus an expression for the bonds in the crystalline regions. The authors discuss possible deviations from the model and elaborate further on the oxidation of cellulose.

A better understanding of the mechanisms and the fundamental chemistry of the heterogeneous hydrolysis of cellulose which have an important impact on the kinetic analysis of the ageing process was gained by the work of Stephens et al. (2008). By using gel permeation chromatography and electrospray ionization-mass spectrometry, they studied the molecular weight distribution of cellulose and the production of cellulose oligomers from thermally aged pure cellulose paper (90°C, 50% RH, up to 11688 h). They concluded that although the rate of the bond cleavage was steady, the position of the bond cleavage was not random throughout the process, which can be understood to proceed in three stages. In stage I, amorphous tie chains (that is, the cellulose chains that extend through the amorphous part to adjacent crystalline regions) break once, causing a large decrease to DP and a loss of tensile strength. In stage II, amorphous chains break for a second time closer to the edge of the amorphous segments, causing smaller changes to DP and generating small amounts of free oligomers. At the same time, chains left intact at the first stage continue to break once, causing further decrease to tensile strength. During stage III, the changes in DP are very small, because hydrolysis occurs on the short amorphous segments protruding from

crystals and to the free oligomers. According to the above, "... cellulose hydrolysis occurred at a constant rate throughout the oven-ageing. Hence, the calculated chain breaks beyond stage I are likely incorrect, because of inaccurately determined DP".

It must be stressed that the symbol DP used throughout this review refers to the number-average Degree of Polymerization of cellulose (DP), as can be seen at the definitions in the beginning of this chapter. The DP of natural cellulose samples can be calculated from the formula (Boyd, 1966; Whitmore and Bogaard, 1994; Klemm et al., 1998):

$DP_v \approx DP_w \approx aDP_n$ (26), where DP_v is the viscosity-average DP, DP_w the weight-average DP, DP_n the number-average DP and a is a constant (polydispersity), approximately equal to 2.

The substitution of eq. (26) to the model equation (9) results in a valid equation with DP_w instead of DP_n and a modified rate constant (divided by a , Zou et al., 1996a). The DP_v can be determined from the intrinsic viscosity of dilute cellulose solutions in appropriate solvents according to various methods (see for example the ASTM D 1795-96). The DP can also be determined by direct methods based on various physicochemical properties (Manley, 1963; Klemm et al., 1998): light scattering, sedimentation/diffusion and vapor pressure osmosis. However, these methods are complex, time consuming and demand complicated equipment.

6.2. PROPERTY KINETICS

According to Arney and Chapdelaine (1981), there are significant differences between the study of chemical kinetics on the one hand and property kinetics on the other. The study of chemical kinetics is based on the mechanism of the chemical reaction and has sound theoretical foundation on principal concepts of physical chemistry. On the contrary, the study of the kinetics of a physical property (ill-defined in most cases as are folding endurance and brightness, which are the most commonly used in such studies) of a complex material as paper is empirical and cannot be directly connected to the mechanisms of the chemical reactions occurring during ageing. Nevertheless, empirical rate constants can be determined and associated with the chemical reactions responsible for the property loss.

The usual practice found in the literature for the study of property kinetics is essentially the same used for the study of chemical kinetics. The value of a physical property P is determined at suitable time intervals and a differential expression similar to a kinetic law is assumed to apply (Arney and Chapdelaine, 1981):

$$\frac{dP}{dt} = kf(P) \quad (27), \text{ where } k \text{ is a constant and } f(P) \text{ an integrable function of the property.}$$

By integrating eq. (27), a linear equation of time would be obtained:

$$F(P) \equiv \int \frac{dP}{f(P)} = kt \quad (28)$$

However, the exact form of the function $f(P)$ is generally unknown and eq. (27) has no mechanistic significance. Thus, $F(P)$ cannot be determined by integration and the researcher must find empirically a function that can linearize the experimental data (Browning and Wink, 1968; Arney and Chapdelaine, 1981). The slope of the linear equation is taken to be equal to the empirical rate constant k . From the above presented analysis it is apparent that the plot of the property function versus time must be linear (Browning and Wink, 1968; Gray, 1969), and since no theoretical restriction in the selection of the linearizing function is imposed, simple expressions are often used and the scattering of the data is usually attributed to the experimental errors.

Browning and Wink (1968) and Gray (1969) used the logarithmic function to linearize most of their folding endurance data:

$F(P) = \log \frac{FN_0}{FN}$, $FE = FE_0 - kt$ (29), where FN = number of folds, $FE = \log FN$ = folding endurance and k constant.

A linear dependence on time was found for the logarithm of the zero-span tensile strength and for the specific absorption coefficient in most of the cases by Browning and Wink (1968). Methodologies based on property kinetics have also been used for the study of paper ageing by others (Roberson, 1976; Baer and Indictor, 1977; Gray, 1977; Roberson, 1981; Strofer-Hua, 1990).

Mendenhall et al. (1981) evaluated several empirical and semiempirical equations for the linearization of folding endurance and reflectance (brightness) data, some of them derived from kinetic models based on the premises that the physical changes are caused by chemical changes occurring during degradation. They found that an equation with the general form as shown in eq. (30) was the most appropriate:

$\ln \frac{P}{P_0} = kt^n$, where the optimal values of n fell between 0.5 and 1.0, with an overall meaning 0.68 ± 0.18 and the optimal value closer to 0.5 and 1.0 for brightness and folding endurance respectively.

Another technique (time-ratio technique) for determining relative rate constants based on property kinetics that does not require the linearizing function has also been described (Frank, 1962; Sizmann and Frank, 1963; Arney and Chapdelaine, 1981). Two identical samples are aged under different conditions until the same value of property P is reached. Then, eq. (28) yields:

$\frac{k_2}{k_1} = \frac{t_1}{t_2}$ (31), where subscripts 1 and 2 refer to ageing under conditions 1 and 2.

By selecting one of the conditions, for example condition no. 1 as reference, then the ratio $\frac{t_1}{t_2}$ can

be taken as a relative rate constant, equal to k in eq. (27) divided by the value of k under the reference conditions. In order to use the time-ratio technique, the form of the function $f(P)$ must be the same at conditions 1 and 2 (Gray, 1977; Arney and Chapdelaine, 1981), which happens if the time ratio is independent of the degree of degradation. The time-ratio technique has been used for the study of the influence of acidity (Arney and Chapdelaine, 1981; Arney and Novak, 1982) and of the relative importance of atmospheric oxidation (Arney and Jacobs, 1979, 1980) in the accelerated ageing of paper.

6.3. ARRHENIUS STUDIES - PAPER PERMANENCE PREDICTIONS

The technique used for the Arrhenius studies is based on the determination of the rate constant k at different temperatures (by the methods presented before, that is, either by kinetic models based on inverse DP or by property kinetics) and the subsequent plotting of the values of k against the inverse temperature. According to the Arrhenius equation (4), the activation energy E_a and the frequency factor A can be calculated from the slope and the intercept of the Y axis of the plot by applying linear regression. Thus, the linearity of the Arrhenius plot is an essential condition for the

application of this technique (Browning and Wink, 1968; Gray, 1969; Roberson, 1981; Zou et al., 1996a).

Concerning the practical significance of the activation energy, it is a measure of the temperature dependence sensitivity of the reaction rate constant: the higher the E_a , the higher the temperature dependence of k . It has been shown that humidity, pH and the physical structure of cellulose affect the pre-exponential factor, while the mechanism of the reaction (whether the degradation process is oxidative, hydrolytic or pyrolytic and to what extent) the activation energy (Zou et al., 1996a; Calvini and Gorassini, 2006; Gilbert et al., 2008). Therefore, the calculated values of E_a and A vary according to the conditions of ageing, the property used for the determination of the rate constant, the composition of paper and the origin of cellulose. Browning and Wink (1968) found values of E_a around 126 KJmol^{-1} (determined from folding endurance) for 3 different papers and Gray (1969) values ranging from 84 to 117 KJmol^{-1} (determined from various physical properties). Shafizadeh and Bradbury (1979) reported for cotton cellulose values of E_a of 88 KJmol^{-1} for ageing in air and of 113 KJmol^{-1} for ageing in nitrogen. Ageing temperatures ranged between 150 and 190°C and the determination was based on inverse DP. In the Barrow laboratory, the mean value of activation energy calculated from 35 experiments based on folding endurance loss was around 106 KJmol^{-1} , with the 72% of values within 8 KJmol^{-1} from the mean (Roberson, 1981). Emsley and Stevens (1994), in their review on the kinetics of low-temperature (90-200°C) degradation of cellulose, applied statistical analysis to previously published data for degradation under various conditions, in order to determine means of activation energy and pre-exponential factors. The mean activation energy was $111 \pm 6 \text{ KJmol}^{-1}$. Five pre-exponential factors were determined, corresponding to 5 sets of experimental setups, according to their potential of oxidation and the susceptibility of cellulose to degradation. The analyzed data were based on inverse DP and the majority of them obeyed the Ekenstam equation (eq. 9). The conditions of ageing were quite diverse but the temperature ranges started from the upper limit of the temperatures used for accelerated ageing tests. Zou et al. (1996a) reported values of E_a and A of 104 ± 3 , 111 ± 4 , and $113 \pm 5 \text{ kJ/mol}$ and 6.41×10^{10} , 1.23×10^{12} and $3.89 \times 10^{12} \text{ days}^{-1}$ respectively for a bleached bisulfate pulp and two bleached kraft pulps. The activation energies were in the range of the reported values of the activation energy for acid-catalyzed hydrolysis (113-117 kJ/mol , Daruwalla and Narsian, 1966), lending further support to the tenet that acid-catalyzed hydrolysis is the main degradation reaction during thermal accelerated ageing. Shahani et al. (2001) and Kaminska et al (2001) performed accelerated ageing in three configurations, that is, in loose sheets, stacks and sealed tubes at temperatures of 70, 78, 84 and 90°C and found linear Arrhenius plots. The determined values of activation energy ranged between 165 and 80.2 kJ/mol , depending on the property used for the determination of the rate constant, the composition of the paper and the configuration of ageing. The value of E_a determined from inverse DP for an alkaline paper aged in sealed tubes was 108.1 kJ/mol (Shahani et al., 2001) and for an acidic paper 106 kJ/mol for single sheet and 118 kJ/mol for the stack (Kaminska et al., 2001). Gilbert et al. (2008) reported a value of E_a of $103 \pm 3.7 \text{ KJmol}^{-1}$ for thermal ageing of kraft paper in oil, determined from inverse DP.

The main objective of the Arrhenius studies has been the prediction of paper permanence. Indeed, the method has been utilized extensively for that purpose and several researchers have proposed various correspondence factors between durations of natural and accelerated ageing (Browning and Wink, 1968; Roberson, 1981). For example, according to Roberson (1981) “68 years of natural ageing correspond to three days at 100°C, which was higher than the 25 years Barrow used in an earlier work, the 28 years reported by van Royen, and the 18.5 and the 20.5 years calculated from the data produced by Wilson and Basch and it is considerably lower than the 306 years calculated from the 30Kcal/mol activation energy suggested by Browning and Wink”.

Nevertheless, the method has also raised objections concerning its precision and applicability in the case of paper and cellulose ageing (Strofer-Hua, 1990; Bansa, 1992; Shahani, 1995; Porck, 2000).

Browning and Wink (1968) studied the reliability of accelerated ageing tests with Arrhenius studies for the estimation of permanence of paper by using 5 different temperatures between 60 and 120°C. The Arrhenius plots of the three properties tested (folding endurance, zero span tensile strength, specific absorption coefficient) were approximately linear. The authors suggest that their results demonstrate the validity of accelerated ageing in ranking papers according to their permanence, but hold the opinion that because of the inhomogeneity of paper and the dispersion of the conventional methods of the determination of paper properties, the absolute assessment of paper permanence is not feasible. For example, for a certain paper the time needed for a reduction in folding endurance to half of its original value was 1529 years, with a range of 97 to 24173 years at 95% confidence level.

The reliability of the TAPPI T 453 accelerated ageing standard (105°C for 72 hours) was studied by Gray (1969) with the aid of the Arrhenius equation. Papers with various additives and compositions were ranked according to their permanence by applying this standard. At the same time, the rate constants of the change of various physical properties of the same papers were determined by dry and humid ageing at various temperatures. The humidity was prearranged so that the moisture content of the samples was around 5%. The results were used for the determination of the ageing rate at room temperature with the aid of the Arrhenius equation and the papers were again ranked according to their permanence. This time the ranking was different, indicating that the TAPPI standard cannot rank properly products with different activation energies. The author points out that a single-temperature test implies that all papers compared have equal activation energies and their Arrhenius plots are parallel.

In a newer study, Gray (1977) discusses the use of the Arrhenius equation for determining the activation energy from the decrease of various physical properties of paper (mainly of the folding endurance) after accelerated ageing. He points out the superiority of the determination of the activation energy by multi-temperature experiments to the single-temperature experiments, as far as the ranking of papers according to their permanence is concerned.

The issues pertaining to accelerated ageing and especially the use of the Arrhenius equation for permanence predictions are very eloquently discussed by Strofer-Hua (1990). The author points out that the margins of error in the determination of the rate constants are high and multiply further in the determination of activation energy, so that the permanence predictions become useless. For example, he uses the upper and lower limits of the activation energy determined by Browning and Wink (1968) and calculates that the higher E_a results in a prediction of 43,000 times longer life than the lower one. He also suggests that extrapolations based on single temperature ageing experiments are not reliable, since as a rule different papers have different activation energies and the Arrhenius plots intersect. If the intersection occurs between the temperature of the ageing experiment and the ambient temperature, the ranking found at elevated temperature is reversed at ambient temperature. On these grounds, he suggests that the temperatures of ageing should not be high if the extrapolations are to be trusted at all. He also points out that even differences in the history of paper may have a bearing in their ageing behavior, which implies that it is practically impossible to derive “universal quantitative rules from accelerated ageing”. Some of the most important objections against the use of accelerated ageing for paper permanence predictions are reviewed by Shahani (1995). Calvini and Gorassini (2006) and Shahani et al. (2001) also elaborate on the uncertainty of the absolute predictions based on the Arrhenius treatment.

Zou et al. (1996a) presented theoretical evidence that the Arrhenius tests methodology applies to paper ageing, even if the degradation is the result of the sum of various reactions having hydrolytic, oxidative or pyrolytic nature with very different activation energies, provided that the conditions of ageing that influence the frequency factor are kept the same for all the temperatures used, and this was supported by his experimental results. For the prediction of permanence, they used the following equation:

$t_{\text{life}} = \frac{1}{A} \left(\frac{1}{DP_{\text{final}}} - \frac{1}{DP_{\text{initial}}} \right) \exp\left(\frac{E_a}{RT}\right)$ (32), where t_{life} the useful life of insulation paper, needed to reduce the initial DP (DP_{initial}) to the final value (DP_{final}) of 200, below which all mechanical strength is lost.

Equations derived by various modifications of the Arrhenius equation, often combined with various kinetic models, have been proposed by several authors for the determination of the absolute permanence of paper (Emsley and Stevens, 1994; Kaminska et al., 2001; Ding and Wang, 2005).

Another method for permanence prediction, also based on the Arrhenius equation has been proposed by Ding and Wang (2007). The Time - Temperature Superposition method (TTSP) is based on the concept that time and temperature are equivalent concerning their effect on ageing, In other words, the same extent of degradation that can be obtained by ageing at a certain temperature for a certain time can be also achieved by ageing at higher temperature and shorter time. The curves of the measured property against the logarithm of time can be superimposed by shifting along the time axis, and the superimposed curve is called the master curve. The shift factor is defined as:

$a_T = \frac{t_{\text{ref}}}{t_T}$ (33), where t_{ref} is the test time at a reference temperature T_{ref} and t_T is the time required to produce the same degradation at temperature T . The shift factors are determined empirically.

By combining eq. (33) with the Arrhenius equation (3), eq. (34) is obtained:

$$a_T = \exp\left[\frac{E_a}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right)\right], \quad (34)$$

Ding and Wang (2007, 2008b) used eq. (34) to determine the activation energy and then fitted the master curve by non linear regression to equations (9) and (24), depending on the choice of kinetic model. Permanence prediction is accomplished by calculating the shift factor at the desired temperature by eq. (34) and then using the fitted master equation to calculate the time necessary to reduce DP to a certain value. The linearity of eq. (34) is required for the method to be valid.

7. ACCELERATED AGEING METHODS

The accelerating effect of elevated temperatures on the rate of paper ageing has been early recognized and the dry-heat treatment was suggested as the means to artificially intensify the degradation of paper (Herzberg, 1899). Based on research at the Swedish Government Testing Institute and the National Bureau of Standards and the work of Gosta Hall, the first standard concerning the accelerated ageing of paper was established (TAPPI T 453; Wilson and Parks, 1983; Porck, 2000). This standard, which survives until today, specifies the use of dry heat treatment (105°C in a ventilated oven) in order to accelerate the ageing of paper. The recognition of the effects of moisture and the need to simulate natural ageing as much as possible led to the

introduction of moist ageing. When the importance of the retention of the acidic volatile degradation products of paper ageing became evident, the use of sealed vessels was introduced and incorporated in a recently proposed standard (ASTM D 6819-02, 2002). The relevant research efforts have been discussed earlier in this review. Notwithstanding the existence of standardized methods, an investigation of the relevant literature reveals that a multitude of proprietary accelerated ageing methods has been employed (Porck, 2000; Zervos and Moropoulou, 2006). Apart from TAPPI 453, other standards that have been widely used include:

ISO 5630-1: Dry heat treatment, identical to TAPPI 453

ISO 5630-2: Moist heat treatment at 90°C and 25% RH. A procedure is described for maintaining the desired conditions in the ageing chamber.

ISO 5630-3: Moist heat treatment at 80°C and 65% RH. A procedure is described for maintaining the desired conditions in the ageing chamber. It has been by far the most popular.

TAPPI T 544: Moist heat treatment at 90°C and 25% RH, identical to ISO 5630-2. A procedure is described for maintaining the desired conditions in the ageing chamber.

ASTM D 6819-02 (2002): A newly developed standard, specifying the use of sealed tubes at 100°C for 120 hours. The preconditioning of the samples at standard conditions is required before sealing the tubes. The ratio of the mass of paper to the volume of the tube is strictly specified. In this test, a single-temperature single-withdrawal ageing test is described for permanence predictions⁶. The permanence of the sample paper is determined by the residual values expressed as a percentage of folding endurance and tearing resistance. The tested papers are classified in two permanence categories (stable or unstable).

ASTM has recently proposed two standards for non-thermal ageing of paper:

ASTM D 6789-02 (2002): Light ageing (Atalla et al., 2000; Forsskåhl, 2000)

ASTM D 6833-02 (2002): Pollution ageing. (Reilly et al., 2000)

8. APPLICATIONS OF ACCELERATED AGEING

The main application of accelerated ageing, as far as paper and cellulose are concerned, is the relative or absolute prediction of paper permanence. Three trends have appeared so far, each with its own advantages and limitations (Kaminska et al., 2001):

- Ageing at a single temperature for one time interval. At the end of the ageing, selected properties of the sample are determined and the permanence of the paper is judged according to their retention. Economic and fast, the method has been criticized on the grounds that papers with different activation energies may not be ranked correctly (Gray, 1969, 1977). Nevertheless, after extensive research, it is recommended in a newly developed standard (Kaminska et al., 2001; Shahani et al., 2001; ASTM D 6819-02; Begin and Kaminska, 2002).
- Ageing at a single temperature for several time intervals. The permanence ranking is based on the degradation rate, determined from the properties loss. More time and labor

⁶ It is remarkable that after several decades of controversy over the efficiency of ageing at one temperature and for one interval and the trend to use more sophisticated methods based on Arrhenius studies and involving mathematical manipulations of various model equations, we return to the starting point by adopting a single-temperature single-withdrawal ageing test for permanence predictions!

consuming, the method suffers from the same disadvantage presented above for the single temperature - single interval approach but presents the advantage that the ageing profile of the sample is determined. Calvini and Gorassini (2006) suggest that the ageing experiment must continue until the LODP is reached.

- Arrhenius studies. The method has been discussed extensively in a previous relevant chapter. Here, it suffices to repeat that because of its low precision and of the reservations expressed about its applicability to paper, its results are of no practical use for absolute predictions (Browning and Wink, 1968; Strofer-Hua, 1990; Shahani et al., 2001). In addition, since the method is costly and time consuming, it has not been included in a newly developed standard (Kaminska et al., 2001; Shahani et al., 2001; ASTM D 6819-02; Begin and Kaminska, 2002)

According to Calvini and Gorassini (2006), although accelerated ageing cannot predict quantitatively the life expectancy of paper, it can still predict “where our paper samples are going”. Semiquantitative predictions that rank papers in two or three general categories (papers with good, medium and poor permanence) are definitely possible, and this is the rationale behind the ASTM D 6819-02 accelerated test standard proposition (Kaminska et al., 2001; Shahani et al., 2001; Begin and Kaminska, 2002). Permanence standards were until recently based mainly on manufacturing specifications⁷ and not performance (ISO 9706; ISO 11108). After a long controversy over the matter, ASTM D 6819-02 introduces criteria based on the performance of the tested paper in an accelerated ageing test. Calvini and Gorassini (2006) also point out that accelerated ageing tests can help in elucidating and understanding the mechanisms responsible for the degradation of paper. They also suggest that accelerated ageing techniques are useful for introducing changes to paper samples in order to set up reliable methods of analysis of authentic materials, and for the evaluation of the kinetic path of paper degradation.

Accelerated ageing has been used extensively for the evaluation of conservation treatments, and the interested reader is referred to relevant reviews (Porck, 2000; Zervos and Moropoulou, 2006). It has also been used for the testing of the influence certain parameters in paper production (such as fiber sources, additives, and procedures) exert on the permanence of paper (see for example: Leclerc and Flieder, 1992; Uyeda et al., 1999; El-Saied et al., 2000; Inaba et al., 2002). Also, for the preparation of samples that emulate aged paper in a controlled manner (Sclawy, 1981; Porck, 2000; Calvini and Gorassini, 2002b, a; Zervos, 2007c).

9. FUTURE OUTLOOK

The abundance of research reviewed concerning the ageing of paper and cellulose indicates the interest of the scientific community in the subject. Several breakthroughs have been achieved, one of the most important in our opinion being the confirmation of the correlation between natural and thermal accelerated ageing by the ASTM research program on accelerated ageing (Shahani et al., 2001). Nevertheless, several issues remain that need further research and clarification. The list that follows highlights some of the most important issues and research perspectives, most of them having been pointed out by other researchers too:

⁷ For example, ISO 9706 specifies a minimum acceptable tearing resistance and alkali reserve (>2% if CaCO₃), a maximum kappa number (an indication to resistance to oxidation) of 5 and a range of acceptable pH (7,5 to 10). No accelerated ageing test is included in the standard.

- The existence and nature of weak links (Feller et al., 1986; Emsley and Stevens, 1994; Calvini and Gorassini, 2006)
- Natural ageing experiments, including measurements of paper properties at intervals of several years, with the objective of determining quantitative relationship between natural and accelerated ageing at defined conditions for defined papers. The matter is being pursued by the Library of Congress (LOC, Shahani et al., 2001).
- Further research on the elucidation of the reactions and the mechanisms involved in natural and accelerated ageing. Determination of all products, connection of products with paper composition and conditions of ageing. The matter is also being pursued by LOC (Shahani et al., 2001) and other research teams (Lattuati-Derieux et al., 2006).
- Elucidation of the mechanisms of degradation and the role of oxidation in the ageing of alkaline and (over)deacidified paper.
- Determination of the importance of the contribution of physical ageing to the ageing process (Fellers et al., 1989).
- Development of non-destructive and miniaturization of existing techniques for the characterization of paper and cellulose (Strlič and Kolar, 2005).

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