

Evaluating and enhancing paper stability – needs and recent trends

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Summary

In the last few years, research in paper stability and conservation has made considerable progress. Some huge gaps in our knowledge can still be identified, where the authors believe more research is needed in the future. Following the identification of major factors affecting paper stability, a closer look is taken at most of them. Paper pH, the role of acids, lignin, atmospheric pollutants and transition metals, photodegradation, atmospheric oxidation, removal of soiling, methods to counteract paper acidity including mass deacidification, and accelerated ageing methods are discussed. While the nature of paper degradation may be of a physical or biological nature, it is the long-term chemical degradation that probably requires the most sophisticated conservation techniques and input in terms of research and funding, and is therefore stressed here.

Introduction

It is difficult to define paper stability, as it depends on the user's expectations – wrapping paper perhaps meets them if it disintegrates as quickly after use as possible, whereas we hope for the paper used in historical documents to last for many centuries. Unfortunately, being a predominantly organic material, it will eventually degrade in even the most favourable conditions, though advanced conservation methods may be able to shift this event far into the future. For most documents, physical properties are the most important aspect; although for documents of aesthetic value, the visual aspect plays a very important role, as well. The question of stability is therefore inherently connected to the degradation rates of these properties – and these rates can be readily and objectively expressed in numbers by researchers.

Paper has been mankind's silent companion for the last two thousand years. Nevertheless, few realise how complex a material it really is: the intricate web of fibres with sizing may, depending on the purpose, contain fillers, coatings, pigments etc. Printing, writing or the application of paint only add to the complexity, so that studies of degradation of such a material demand a complex experimental approach (BARAŃSKI, 2002). From the most simplistic viewpoint, however, paper can be regarded as *cellulosic fibres with additives*. There is a good reason for this: in order to be able to study the stability of such systems, researchers need to work with models.

Factors affecting paper stability

A simplified scheme of factors affecting the degradation rate of cellulose is given in the self-explanatory Figure 1. One should be aware, though, that in the course of time, the migration of paper components, degradation products (especially volatile organic compounds), or pollutant gases (e.g. SO₂, NO_x) additionally contributes to the complexity. Recent studies of the ageing of paper in stacks have shown how important it is to take this aspect into consideration (CARTER, 2000). In the following paragraphs, most of the issues will be addressed separately. Since a comprehensive review was published in 2000 (PORCK, 2000-1), the present text will attempt to outline the more recent achievements in paper conservation chemistry.

The measure of things...

Not long ago it was demonstrated (ZOU, 1996-1) that physical properties (retention of fold endurance) of pulp sheet samples correlate with the average length of cellulosic macromolecules, expressed by the number of monomers, *i.e.* *degree of polymerisation* (DP). Although the correlation between retention of physical properties and DP is not linear, studies of the latter lead to valid conclusions regarding physical stability. This justifies the use of chemical methods of characterisation of cellulose (determination of DP) in-

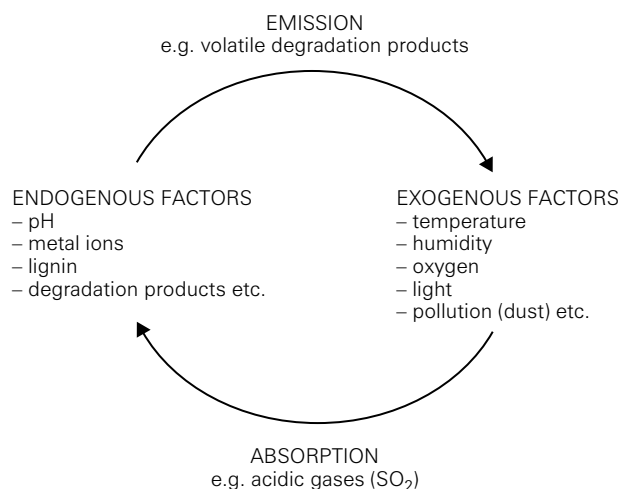


Figure 1. A simplified scheme of factors affecting paper stability.

stead of characterisation of physical properties. This is important, because DP determination, especially viscometry, is less time-consuming, less of a sample is needed and measurements are in general more reproducible than the determination of any physical property (*e.g.* fold endurance, tensile strength, etc.). In addition, standard viscometric methods exist for the determination of DP [*e.g.* ISO 5351/1].

Being a natural macromolecular material, all cellulose molecules are not of the same DP and occasionally, instead of an *average* DP value, its *distribution* is needed. A recent example was a size exclusion chromatographic study (SEC) of changes in DP incurred by the laser cleaning of paper (KOLAR, 2002), which could not have been adequately described using viscometry alone. SEC (for a review of the technique see STRLIČ, in print-1) is time-consuming and the data are less reproducible than viscometric data. Besides this, SEC suffers from some systematic errors which are difficult to evaluate (STRLIČ, 2002). Viscometry, on the other hand, may yield an underestimated DP of heavily oxidised cellulose (STRLIČ, 1998) although in such cases a reductive pre-treatment can be used.

Two aspects, however, still deserve additional attention. It was proposed in 1999 (PEDERSOLI, 1999) that a proper miniaturisation of DP determination should be attempted in order to be able to take samples of original material in a micro-destructive manner (single fibres), and a micro-SEC method has been further proposed (STOL, 2002). In principle, viscometry could also be miniaturised and some level of automation introduced in order to increase samples throughput.

The Models

As sources of pulp fibres, modern cotton linters (*e.g.* Whatman filter paper) and bleached wood pulps are most often used. The use of generally and commercially accessible models, such as Whatman filter paper, should be encouraged in order to ensure that experiments are repeatable and controllable. Bleached wood pulps are also frequently used models. However, the pulps used for the production of historic materials were of quite a different origin, and while data obtained with bleached wood pulps are valuable, they may not be entirely representative of all types of historical paper, as they contain materials alien to, for example, rag paper, such as hemicelluloses (with a higher content of carbonyl groups) and lignin, which can alter the course of degradation considerably as compared to pure cellulosic material (MALEŠIČ, 2002). One should therefore be cautious in generalisations. During the production of models, the introduction of non-cellulosic material is most often performed by immersion.

Paper pH

Paper pH is not a well-defined parameter, although many standard methods exist for its determination, either of the pH of paper surfaces using flat electrodes [TAPPI T 529 om-88] or of paper extracts [TAPPI T 252 om-90]. While measuring surface pH may be a satisfactory procedure for models, it leaves watermarks on originals where degradation proceeds more quickly. Besides the use of micro-sampling (*e.g.* micro-drilling, WESS, 2001), miniaturisation of the very measurement procedure is also called for, *e.g.* the use of microelectrodes or of a spectroscopic method. Additional justification for this stream of research is the fact that cellulose fibres contain only approximately 5% water (in the so-called amorphous regions up to 17%); its mobility, as well as the mobility of additives, is limited, probably leading to some distribution of pH in the material. It is not possible to overestimate the problem of pH determination, as it is well known that acidity in paper (introduced in papermaking in 1807) has led to catastrophic situations in most modern libraries.

Acid hydrolysis

It is well known that cellulose degrades in acidic media, and numerous studies have been published on the subject, including two authoritative papers by Zou *et al.* (ZOU, 1996-1 and 2) who showed that the rate of degradation increases with acid concentration in a linear manner. The mechanism of degradation is such that during the chemical reaction, acids are not consumed but rather catalyse bond scission. Since additional acids are formed in side reactions, acid-catalysed degradation is actually autocatalytic (*i.e.* self-accelerating). Many 19th and 20th century historical documents are in danger due to this type of degradation. However, effective conservation treatments have been proposed. Immersion into solutions of $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{HCO}_3)_2$ or $\text{Mg}(\text{HCO}_3)_2$ are the most frequently used aqueous conservation treatments (*deacidification*) – the acids are thereby neutralised and an additional amount of alkali is deposited in the paper forming the *alkaline reserve*, which is to counteract acidity to be formed during the future degradation. For several types of documents (*e.g.* with water-sensitive inks), non-aqueous deacidification procedures have been developed, the active (alkaline) Ca and Mg components being soluble in organic solvents and supposedly turning into their respective carbonates after the evaporation of the solvent and the reaction with atmospheric CO_2 . The problems associated with these methods are that the by-products of acid-catalysed degradation (*e.g.* glucose) are not washed out of the treated object, and that many alkaline active constituents are too reactive (*e.g.* alkoxides) or turn into their respective carbonates too slow-

ly. The remaining degradation by-products, impurities in and side reactions of deacidification substances and high alkalinity may cause faster degradation during the subsequent ageing of the deacidified material (KOLAR, 1998 and in print).

Mass deacidification

While manual deacidification is effective, the extent of the problem is such that methods used to deacidify large quantities of materials in a single batch were developed and are applied in several countries on a regular basis (for a recent review see BLUHER, 2001). A successful treatment should neutralise paper acidity, leave a uniform and sufficient deposit of alkaline reserve, should not harm any library material, and should not change paper appearance or physical properties. However, due to the sensitivity of library materials to water and due to the time and energy consuming drying processes, non-aqueous solvents are usually used. As a result, the alkalis are either finely-powdered CaCO_3 , CaO or MgO or compounds of Zn, Ti, Ca or Mg soluble in various solvents. Since most solvents in current use are costly or harmful, studies for their recovery or replacement with environmentally-friendly chemicals (*e.g.* supercritical CO_2 , a method using this liquid with CaCO_3 as the deacidification agent already described in (SELLI, 2000) should be encouraged. Several large projects on national levels were financed in the past, however, the interest in the mass deacidification recently somewhat decreased due to the obvious benefits of deacidification in general. Unfortunately, none of the current mass treatments fully satisfy the above criteria and cautions have recently been expressed. Some of the treatments leave a visible surface deposit and cause unwanted yellowing of mass-deacidified model papers during subsequent accelerated ageing (KOLAR, 1998 and in print) when compared to untreated materials. Additionally, some non-aqueous deacidification treatments lead to excessive paper alkalinity ($\text{pH} > 9.5$), which destabilises the treated object due to degradation reactions promoted by high alkalinity, *i.e.* alkaline degradation and oxidation.

Oxidation

Alkaline degradation and oxidation are fundamentally different processes. The former constitutes a series of degradation reactions, in which the presence of oxygen is not a prerequisite and proceeds in the oxidised cellulose macromolecule in places where oxidised functional groups (carbonyl groups) have formed. Elimination and a series of subsequent isomerisation reactions lead to bond scission and the production of acids.

In the case of oxidation, the presence of atmospheric oxygen is needed. In many organic materials, it proceeds in an autocatalytic chain reaction (*autoxidation*) involving free radicals. The concept of the radical chain oxidation of organic compounds is known from the late 1940's, and was discussed in relation to paper stabilisation in 1997 (KOLAR, 1997). The presence and build-up of free radicals (KOLAR, 2001) and hydroperoxides (KOČAR, 2002) during the ageing of cellulose has also recently been demonstrated. The rather complex set of autoxidation reactions was presented in (KOLAR, 2000-1) and the possibilities of usage of compounds which would be capable of slowing down the autoxidative reaction route (*antioxidants*) was discussed. These can be classified according to their mode of action as *preventive antioxidants* (discussed in detail in STRLIČ, 2001-1) *free radical scavengers* (discussed in KOLAR, 1998) or *antioxidants synergists*. However, the best results so far were obtained using iodide as a heterolytic peroxide decomposer. After reduction of oxidised groups in cellulose, deacidification and introduction of KI, practically no degradation of paper was determined after a 40-day accelerated ageing period at 80°C , 65% RH (KOLAR, 1998). It would therefore seem that a paper conservation treatment providing almost indefinite stabilisation is just a footstep away, though thorough testing of many additives for possible side effects under photo- and thermal ageing conditions is yet to be performed.

Transition metals

In the autoxidation reaction scheme, transition metals play an extremely important role, as they catalyse the production of free radicals from hydroperoxides, the intermediate reaction products of atmospheric oxygen and organic matter. This catalytic reaction can be interfered with by the introduction of complexing agents that deactivate the transition metal (either by changing its reductive/oxidative properties or by making it inaccessible to hydroperoxides). Such compounds are classified as preventive antioxidants. The important role of transition metals will be addressed in the 'MIP' 5th Framework thematic network.

The content of transition metals in most cellulosic materials is low enough not to present an acute problem (although their content in paper increased after Hollander beaters were invented at the end of the 16th century). However, in certain inks (especially *iron gall ink*, although a more appropriate term, *metal tannate ink*, was recently suggested) and pigments, large amounts of iron and copper are present, and may lead to extensive localised degradation to such an extent that many historic documents are simply not legible any-

more. In order to appreciate the seriousness of the problem, it should be stressed that many manuscripts (*e.g.* Leonardo da Vinci's), musical scores (*e.g.* J. S. Bach's) and drawings (*e.g.* Rembrandt's) were made with iron gall ink. With the aim to propose a non-aqueous conservation treatment for such documents, the 5th Framework project 'InkCor' was launched in 2002.

The natural compound phytate was proposed as a key preventive antioxidant in aqueous treatment some time ago (NEEVEL, 1995). Its use was later evaluated and optimised, also in (KOLAR, 2000-1), although it is not certain to what extent (and in what way) it is able to stabilise the numerous copper-containing metal tannate inks – copper is namely known to catalyse free radical production much more efficiently than iron (STRLIČ, 1999). Furthermore, in non-aqueous conservation treatment, phytate cannot be used due to limited solubility. Further research into metals other than iron and into the use of alternative antioxidants (or 'cocktails' thereof) is therefore needed.

Lignin

Historically, lignin was considered to be one of the major reasons for the rapid deterioration of the physical properties of lignin-containing paper. However, it has recently been demonstrated that the main factor affecting its stability is acidity, and that lignin does not have a negative impact, providing the paper contains a sufficient amount of calcium carbonate (BÉGIN, 1998). This finding led to a new Canadian Standard, 'Permanence of Paper for Records, Books and Other Documents', in September 2000 [CAN/CGSB-9.70-2000]. It has even been suggested that lignin may act as a hindered phenolic antioxidant, thus protecting cellulose during ageing (BARCLAY, 1997).

However, the light-sensitivity of this group of antioxidants is well known and material discolouration is the result of exposure to light. Certainly, lignin is no exception (BUKOVSKY, 2000). Lignin's most undesirable feature thus remains its adverse effect on brightness stability of paper, and considerable research has lately been dedicated to the topic. As a result, numerous compounds have been found to be efficient inhibitors of photo-induced brightness reversion of mechanical pulps (FORSSKAHL, 1996; BEYER, 2001). This research will prove useful for the development of suitable conservation treatments for lignin-rich paper, an increasingly often used material for works of art, which should exhibit an enhanced light stability.

Absorption of atmospheric pollutants

From the atmosphere surrounding archival material, gases such as SO₂, NO_x or volatile organic acids can be absorbed. Their role has already been studied extensively (JOHANSSON, 2000-1 and 2). As a conse-

quence, filtration systems have been installed in many repositories (DE FEBER, 1998). While gases coming from an external source can be eliminated this way, another aspect of the problem, *cross-contamination* from internal sources (*e.g.* unstable material being kept in close proximity of another), should also be addressed. The phenomenon is sometimes called *infectious spreading*, a term adequately borrowed from medicine. The migration of volatile degradation products (especially acids) is known to take place within stacks of paper (CARTER, 2000; BULOW, 2000) and the formation of carbonyl compounds (promoting autoxidation) has also been followed (LEVART, 1999). While the former leads to consumption of alkaline reserve, the latter probably leads to the initiation of oxidation reactions. The removal of volatile acids from the atmosphere has been attempted by using commercially available sheets with an integrated layer of sorbent, with controversial results (DANIEL, 1999). Optimisation and thorough testing of these products is needed, as *passive conservation* methods are increasingly used by the conservation community and represent the preferred method of 'treating' objects for which an adequate active conservation technique is not yet available.

Soiling

While it is difficult to determine what type of paper soiling bears information or represents patina to be preserved, foreign particulate matter (*e.g.* dust) is generally unwanted from a chemical point of view, as it may contain catalytically active compounds, is hygroscopic, and may provide food, and thereby a growth medium for microorganisms. In traditional techniques of cleaning, wet or dry, unwanted alterations of surface structure or composition may occur as a consequence of physical contact with the artefact. For chemically sensitive or physically fragile materials, however, laser cleaning offers certain advantages, since material handling can be minimised. Besides, unprecedented spatial accuracy can be achieved. This was first reported in 1994 (SZCZEPANOWSKA, 1994). However, the use of excimer lasers was later discouraged due to excessive laser-induced degradation (KOLAR, 2000-2), while studies with Nd:YAG laser are continued within Eureka E!2541 'Renova-laser' and Craft 'PARELA' European projects and COST G7 action. The degradation of clean models during laser treatments seems to be limited to long-term destabilisation, while severe yellowing can be observed in some cases when cleaning of soiled surfaces is attempted (KOLAR, 2002). The discussion as to the source of the yellowing phenomena continues (STRLIČ, in print-2), though it seems that thermal degradation products are the cause. While it is doubtful that laser cleaning will ever be applicable as a general method for the clean-

ing of larger paper areas, it might become indispensable for cleaning very delicate artefacts (*e.g.* tears) or areas otherwise inaccessible (*e.g.* three-dimensional objects).

Photodegradation

Although extensive research has been devoted to the mechanisms and possible colour stabilisation of lignin when exposed to light, not much is known about the effects of light on cellulose or paper made from bleached chemical pulps. Cellulose is in general considered to be quite stable when irradiated by daylight, and in a recent study lignin-free paper lost its optical properties slowly and was considered to be stable, although changes in fluorescence were observed in the initial phases of light ageing (ARNOLD, 2002). However, all papers involved in the study suffered a loss of mechanical strength to a considerably greater degree than expected during long-term natural ageing. This behaviour was observed also for pure cellulose (Whatman filter paper) during 35 days of exposure to daylight (BUKOVSKY, 2001). Deacidification using methoxy magnesium methyl carbonate was able to slow down the degradation. In addition to the immediate degradation caused by exposure to daylight, it is expected that the ageing stability of irradiated paper is also impaired (LEE, 1989).

From a mechanistic point of view, not much is known about the reactions leading to light-induced discolouration (*brightness reversion*) and degradation of bleached chemical pulps or cotton cellulose. However, the mechanism is considered to differ from that occurring during thermal ageing (CHIRAT, 1999). Studies of chemiluminescence may provide additional insight into the initial processes (STRLIČ, 2000), and further mechanistic research is planned within the 'PAPYLUM' 5th Framework project.

Although exposure to light is considered to be of minor importance for general archival and library collections, its effects on the most precious objects, which are often exhibited, should not be underestimated. The subject calls for more in-depth research, in particular with respect to different deacidification treatments.

Accelerated thermal ageing studies

Ageing of cellulose and paper at natural conditions proceeds at rates difficult to determine unless extremely long experimental times are granted. Since reaction rates are generally accelerated at elevated temperatures, *accelerated ageing* in climate chambers (at a defined temperature and relative humidity) is performed whenever stability evaluation is attempted. However, this approach has been ques-

tioned due to the fact that not all reactions are accelerated to the same extent (PORCK, 2000-2) and by assuming they are, faulty conclusions may be drawn, as shown in a study of preventive antioxidants for paper (STRLIČ, 2001-1). In other words, in order to be able to extrapolate the rate of degradation to room temperature, accelerated ageing at several temperatures should first be performed. Such studies are time and work intensive and are therefore rarely performed. Furthermore, their value is still limited due to sizable errors associated with mathematical extrapolation.

In acknowledgement of these difficulties, new methods are being developed and tested with promising results, such as sealed-vessel accelerated ageing (BÉGIN, 2002) and studies of weak light emission during atmospheric oxidation of cellulose, which was introduced in 1979 (KELLY, 1979) and then forgotten for almost 20 years (for a review see STRLIČ, in print-3). They can be conducted near room temperature (thereby reducing the extrapolation error) and in addition, they are not time consuming. In fact, typical experimental times are measured in hours, not months, as is the case of accelerated ageing. The introductory work showed that in studies of degradation (especially oxidation) mechanisms, chemiluminescence has proven extremely useful (STRLIČ, 2001-2; RYCHLÝ, 2000). However, for a general correlation between light emission and degradation rate, more work is needed. Recently, a mathematical model was presented for temperatures above 100°C (RYCHLÝ, 2002), giving us cause for optimism. At lower temperatures, humidity plays an important role, so that recently, within the 'PAPYLUM' 5th Framework project, a chemiluminescence prototype was constructed allowing studies in environments of defined humidity and, in addition, allowing for non-destructive sampling.

Stability studies should not only provide an estimation of the stability of historical materials, but also help us to evaluate the adequacy of particular treatments and design new ones. Research in this direction is therefore of primary importance.

Conclusions

It should be stressed that the present text focuses on topics deserving of the most attention according to recognisable trends in literature. Subjects were further chosen in order to stress the areas of paper conservation where significant future input is needed. Recognition of these needs is important, since the participation of chemists, physicists and conservation scientists on an international level is needed to provide high-quality expertise on the individual problems. Additionally, only if supervised and assist-

ed by conservators and collection keepers will the quest for the preservation of the immense wealth of heritage on paper be successful. We can generally outline the development of a method according to the following steps, which simultaneously emphasise the weak points of the process:

Problem identification should be carried out on two levels – while collection keepers and conservators identify phenomena on a macro level, researchers should recognise them on a micro level. This is seldom easy, an especially interesting example being localised yellowing (*foxing*) on paper, where scientists are still not sure as to the reasons for its appearance (BICCHIERI, 2002; PRESS, 2001; ARAI, 2000; CHOISY, 1997). *Micro-destructive and non-destructive methods of analysis* are the key areas of development, as emphasised by the European co-operative COST G8 action. Since specific reactions or reaction systems are targeted in chemical methods of conservation, *studies of degradation and stabilisation mechanisms* are the true basis for method development.

Treatment optimisation and testing should be founded on a sound choice of models and comprehensive photo- and thermal- *accelerated ageing experiments*, which are both time and work intensive, so their development should be encouraged. Many conservation procedures, even those which are regularly used, *e.g. (mass) deacidification*, are in need of such optimisation.

Treatment standardisation is another important aspect, and should involve a consortium of all interested parties. Accepted *conservation treatment directives* should serve as a general guidance to those conservators less interested in research and development.

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