

DEACIDIFICATION FOR THE CONSERVATION AND PRESERVATION OF PAPER-BASED WORKS: A REVIEW

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Embrittlement threatens the useful lifetime of books, maps, manuscripts, and works of art on paper during storage, circulation, and display in libraries, museums, and archives. Past studies have traced much of the embrittlement to the Brønsted-acidic conditions under which printing papers have been made, especially during the period between the mid-1800s to about 1990. This article reviews measures that conservators and collection managers have taken to reduce the acidity of books and other paper-based materials, thereby decreasing the rates of acid-catalyzed hydrolysis and other changes leading to embrittlement. Technical challenges include the selection of an alkaline additive, selecting and implementing a way to distribute this alkaline substance uniformly in the sheet and bound volumes, avoiding excessively high pH conditions, minimizing the rate of loss of physical properties such as resistance to folding, and avoiding any conditions that cause evident damage to the documents one is trying to preserve. Developers have achieved considerable progress, and modern librarians and researchers have many procedures from which to choose as a starting point for further developments.

Keywords: Deacidification of paper; Conservation of documents; Acid-catalyzed hydrolysis; Calcium carbonate; Alkaline reserve; Mass deacidification; Library collections; Aging of paper

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INTRODUCTION

Relentlessly, the forces of degradation are at work on the books, maps, manuscripts, and works of art on paper in storage, circulation, and display within our libraries, museums, and archives. Conservators and conservation scientists strive to slow degradation of heritage materials to retain their intellectual, historic, artistic, and economic worth. Figure 1 shows examples of books that have become brittle and cracked during storage. Various factors affecting such degradation have been reviewed in previous publications (Seeley 1985; Aspler 1989; Gurnagul et al. 1993; Zervos 2010). The topic is of interest not only to those responsible for the preservation of paper-based collections, but also to those dealing with the chemical and physical stability of cellulosic fibers used in other applications.

The goal of the present article is first to highlight a highly significant and vexing mode of paper's degradation, the proton- or Brønsted-acid-catalyzed hydrolysis of cellulose (Baty and Sinnott 2005)—and the effort to stop it—called *deacidification*

(Smith 1970, 1987, 1988; Williams 1971; Mihram 1986; Sun 1988; Lienardy and van Damme 1990; Sparks 1990; Barbe 1991; Zimmermann 1991; Carter 1996a,b; Daniels 1996; Porck 1996; Zappalà 1997; Blucher and Vogelsanger 2001; Zervos and Moropoulou 2006). Our intent is to be rigorous both in terms of the mechanistic chemistry of paper degradation, which the various deacidification procedures are designed to prevent, and also to be rigorous in placing the deacidification procedures in the teleological and historical context of conservation. A further goal is to call attention to publications dealing with a wide range of both practical and theoretical issues related to deacidification. The literature reviewed reveals a richly varied set of motivations, strategies, and observations. These observations can provide opportunities in academic research, serve as the basis for future business ventures in paper preservation, and prompt further development of policies and practices related to deacidification.

The present article is organized as follows: introduction (including motivating reasons for deacidification); factors affecting degradation of paper-based articles highlighting, of course, Brønsted acidity and cellulose hydrolysis; deacidification agents; distribution methods; criteria for judging the success of a deacidification program; associated or alternative treatments; and conclusions.



Figure 1. Examples of 20th century acidic books that have become embrittled during storage. Left: Brittle book with pages detached; Right: Brittle pages separating from binding

Briefly stated, the term *deacidification* denotes the treating of a paper-based object to neutralize its acidic content, with the objective of prolonging the object's useful life. As most deacidification measures also provide a reserve of alkalinity to neutralize acids that may be generated in the future either from within the paper itself, or by introduction from its storage environment, the terms *neutralization* and *alkaline buffering* are also applicable to the discussed treatments. To minimize costs and effort, there can be a strong incentive to treat large numbers of items at once, particularly in the case of bound volumes, where ideally one would not have to remove bindings. A *mass deacidification* program can be defined as an effort to remove acidity from several

hundred or more books at a time (Harris 1979; Arnoult 1987; Morrow 1988; Cunha 1989; Hon 1989; Schwerdt 1989; Sparks 1990; Turko 1990; Lienardy 1991, 1994; McGee 1991; Zimmermann 1991; MacInnes and Barron 1992; Wedinger 1993; Brandis 1994; Harris and Shahani 1994a,b; Wittekind 1994; Kaminska and Burgess 1994; Havermans *et al.* 1995; Kaminska 1995; Liers and Schwerdt 1995; Okayama *et al.* 1996; Porck 1996; Blüher and Vogelsanger 2001; Rousset *et al.* 2004; Banik 2005; Ipert *et al.* 2005).

Although the terms *acidic papers* or *alkaline papers* are pervasive in the literature, these terms are not rigorously defined in terms of solution theory (TAPPI 2002a). Acids and bases, according to the prevailing definition by Arrhenius, are species that introduce either protons or hydroxide ions, respectively, into aqueous solutions. Paper is not an aqueous solution, but a network of hydrophilic, insoluble fibers with adsorbed water molecules. Despite this difference, a useful concept of acidic or alkaline papers has emerged, based on the acidity or basicity of water extracts (TAPPI 2002a; Browning 1997). While the concept of *paper pH*, measured in suspensions of macerated paper in excess water, dates to the 1930s as a “tentative standard” of the Technical Association of the Pulp and Paper Industry (TAPPI 2002b), by the 1970s a *surface pH* measurement was needed, which measures the paper pH nondestructively. Measurements of paper pH are discussed more fully below.

Motivating Reasons to Preserve Paper-Based Heritage Collections

The goal of paper preservation extends beyond heritage materials and includes certain industrial applications, with the degradation of transformer insulation (Heywood 1997) being one example. We will draw on that literature to the extent that it is applicable, but will not discuss it explicitly as we focus on the preservation of archival and library collections, as well as paper-based historic and artistic works, for which the prominent motivations are given in Table 1.

Table 1. Prominent Reasons to Preserve Paper-Based Heritage Collections

Reason	Literature References
Extend the useful life of documents	Schwerdt 1989; McCrady 1990; Sparks 1990; Balazic <i>et al.</i> 2007; McGee 1991
Preserve historical artifacts in their paper-based form	Schwerdt 1989; Turko 1990; McCrady 1990
Preserve evidence suitable for future analysis	Muñoz-Viñas 2004
Protect the value of historical and archival materials	Schwerdt 1989
Achieve specified levels of strength retention when the paper is exposed to conditions of artificial aging	Wilson <i>et al.</i> 1981; Zervos and Moropoulou 2006
Make the contents available to future readers	McCrady 1990

Deacidification is a promising strategy to address objectives listed in Table 1, to block the chemical mechanism of Brønsted-acid-catalyzed hydrolysis of cellulose, and to slow the rate of paper degradation.

The magnitude of the paper preservation problem is perhaps best illustrated by the plight of major libraries, which are charged with the responsibility of extending the useful life of printed material considered to have value in its original form, be it valuable,

historic, or unique. The Library of Congress receives two copies of most books printed in the USA. Surveys of their collection showed that about 25% of items in their collection were so brittle that they were judged likely to fail if sheets were folded (Anon. 1988). The rate at which acidic books deteriorate under typical library conditions has been estimated at about 4.7% per year (Cunha 1987). Note, however, that this estimate is based on a linear extrapolation of folding endurance data to zero strength and may be an underestimate, since recent studies suggest that the rate is not constant, but increases with time. The acceleration is due to autocatalysis, which is oxidation working in tandem with acid-catalyzed hydrolysis to produce a spiraling effect (Shahani 1995; Shahani *et al.* 2001; Zervos and Moropoulou 2005; Zervos 2007; Calvini *et al.* 2007, 2008) on which we elaborate later.

While the extent of acidity within a given volume will be affected by the conditions of storage (temperature, relative humidity (RH), atmospheric pollutants, quality of shelving and boxing materials, *etc.*), the parameters of paper manufacturing are the first and primary causes of Brønsted acidity of paper. Thus, all copies of the same book may be compromised, and purchasing a replacement volume in the market is of little value. As will be discussed in the next section, much of the paper that was manufactured during the period between about 1820 and 1990 will measure as being acidic due to the additives used during its manufacture (Sclawy and Williams 1981; Hubbe 2005). Such paper has been shown to degrade more rapidly if stored at higher humidity and temperature, leading to more rapid chemical breakdown and an increased likelihood of breakage. This is especially the case with books, for which the paper must perform mechanically both within the binding structure and during the turning of pages. Libraries' strategic initiatives for deacidification, reformatting, and replacement copies are therefore based on date-of-imprint reports to estimate the risk of embrittlement. These reports classify time periods of inferior paper manufacture and are used to characterize the "brittle books problem" in major libraries in the US and Europe.

For items of high value, libraries and museums have an even more urgent incentive to maintain favorable conditions during storage. In such cases, the goal is to preserve each item without losing those essential characteristics that make it valuable. For example, if an acidic book is valued because of annotations from a famous individual, the deacidification treatment should not remove, bleed, or otherwise cause any change to those annotations. Thus it may be essential at times to avoid any visible changes to the original appearance during treatment. Nevertheless, as noted by Barrow (1965), the restored, conserved, or stabilized item must be sufficiently strong so that someone can use it; otherwise there may be little point in carrying out the deacidification process.

FACTORS AFFECTING DEGRADATION

What makes life possible on earth is the varied, active, and complex chemistry to which carbon-containing molecules are subject in our atmosphere. Given that the biopolymer cellulose is responsible for a paper's structure, and usually the bulk of its substance, it is hardly surprising that paper may lose its quality over time. Awareness of

paper's vulnerability to degradation has a long history (Murray 1824, 1829; Johnson 1891; MacAlister 1898; Hall 1926; Hanson 1939). Lignocellulosic material can be considered as being unstable from a thermodynamic standpoint (Lindström 1990; Luner 1990; Gurnagul *et al.* 1993). The reaction of the material with oxygen releases considerable heat during such processes as fire (Huggett 1980) or biological decay (Ball 1997; Dougherty 1998).

On the other hand, pure cellulose is chemically a very stable material at ambient temperatures. Books can also be surprisingly permanent and durable. Many *incunables*, books from the “cradle period” of printing, appear as if they have just arrived from the printer, even after 500 years. From this we surmise, as mentioned above, that the permanence of a paper-based object must greatly depend on its initial formulation, as well as the conditions of storage. Figure 2 shows examples of 19th and 20th century books whose initial manufacture had led to their embrittlement, to the point of failure at the point of folding.



Figure 2. Examples of acidic printed items that have failed at the fold. Left: Atlas with acidic paper. Right: Brittle pages separating from a binding

Composition of the Original Paper—19th and 20th Century

Those who purchase paper for the publication of books, periodicals, or for use in offices can select from a variety of specified levels for appearance and various strength properties. As a first rule, many purchasers assume that initially high values of strength characteristics may be the best indication that the paper will remain above a critical threshold of strength, as well as retaining a suitable appearance, in the distant future. At a minimum, it would certainly make sense to avoid use of paper that is already weak or unsightly when it is new. Scott *et al.* (1995) give readers a comprehensive and user-friendly textbook on paper properties. Smook (1991) gives strategies that papermakers use in the selection of the materials, in the preparation of the fibers, and in the forming of the paper in order to meet customer requirements for different applications. Furthermore, the strength of paper can depend both on the strengths of the individual fibers and on the strength with which they are attached to each other (Page 1969). Some important factors can include fiber source (*e.g.* pine, maple, eucalyptus, straw, cotton, *etc.*), fiber dimensions, and wall thickness. To provide context for the discussion of paper working

qualities, Table 2 lists some of the performance requirements that new paper must meet to satisfy expectations of publishers, printers, conservators, and librarians.

Table 2. Essential Performance Attributes of Printed Paper for New Documents

Attribute	Literature References
Resistance to breakage during handling, folding, <i>etc.</i>	Zervos and Moropoulou 2006
Suitable appearance (brightness or color, and uniformity)	Sparks 1990; Kolar and Novak 1996; Bukovský 1997; Sundholm and Tahvanainen 2004
Relatively even, uniform surface for printed images	Scott <i>et al.</i> 1995
Suitable stiffness and thickness (caliper) for the application	Scott <i>et al.</i> 1995
Ability to maintain these features during extended storage	Wilson and Parks 1980

As noted in Table 2, the paper that comprises printed or written documents not only has to be strong enough to resist breakage, but it also needs to retain a suitable appearance, and the original qualities such as formation uniformity and bulk density need to be suitable for the application. Librarians, conservators, and humanists expect contemporary papers to meet the same standards of durability, performance, and permanence as do historic papers made from cotton or flax.

Fiber Processing (pulping, bleaching, fillers)

The kraft pulping process (Smook 1991), which entails removal of most of the lignin from wood, is most often used for the production of modern fine printing papers for books, reports, calendars, *etc.* Cotton, which is sometimes used as a source of fibers for high-quality archival papers, does not contain lignin to begin with. By contrast, mechanical pulping processes, which retain almost all of the solid material from wood in the final product, are widely used for relatively short-lived products, including newspapers and popular magazines. Thermomechanical and groundwood pulps also find their way into products intended to have a longer life, where cost becomes the primary motivating factor. As expected, given the motivations behind each pulping process, the kraft process generally yields stronger paper, and this is largely as a result of higher conformability of the refined fibers while they are in the wet state. The bonding ability and other strength characteristics of kraft fibers comes at a price, however; recycling of paper made from kraft fibers can result in significant losses in bonding ability and related strength characteristics (Law *et al.* 2006; Park *et al.* 2006; Hubbe *et al.* 2007). Factors that make kraft fibers vulnerable to changes during drying, usage, and recycling include their more porous nature (Stone and Scallan 1968; Berthold and Salmén 1997) and an unavoidable loss of cellulose degree of polymerization when fibers are subjected to alkaline pulping and the associated bleaching treatments (Welf *et al.* 2005).

Fibers from mechanical pulping, though they generally retain their strength characteristics well during recycling operations (Law *et al.* 2006; Park *et al.* 2006), are not without problems during long-term storage of paper. In the first place, the initial strength of paper made from mechanical fibers tends to be lower than those of paper made from kraft pulp. The lignin in high-yield pulps is prone to yellowing during storage, especially if the paper is exposed to light or if metal catalysts are present (Rychly *et al.*

2006). Questions have been raised about effects of lignin on the chemical breakdown of cellulose (Anon. 1995a; Bukovský and Kuka 2001). Work by Bégin *et al.* (1998) has largely disproved the idea that lignin, on its own, increases the vulnerability of paper to acid-catalyzed hydrolysis, while still presenting acidity as the most important factor affecting the breakdown of paper. Follow-up work showed that papers made from mechanical pulps tend to absorb more SO₂ from polluted atmospheres compared to paper made from lignin-free fibers, and the resulting acidity can make a minor, but measurable, contribution to the breakdown of the paper (Bégin *et al.* 1999; Tse *et al.* 2002).

Though mineral fillers tend to block potential bonding sites, thereby decreasing paper's strength (Hubbe 2006), their effect on archival quality of paper is more complex. Calcium carbonate, which is presently the most widely used class of filler, tends to neutralize Brønsted acids that are adsorbed onto the paper, or that are generated within the paper itself. This behavior has been dubbed *alkaline reserve buffering* by conservation scientists, which refers to the alkaline salt keeping the pH high until it is exhausted (if it ever is) by acidic species that emerge. An *alkaline reserve buffer* is clearly distinct from a *common-ion-effect buffer*, which keeps the pH at a certain point via le Chatelier's principle. Probably the most common and significant example of the latter in paper history is gelatin sizing, where gelatin, an amphoteric protein, buffers the paper at a certain pH depending on the preparation of the gelatin (Baty and Barrett 2007). Gelatin sizing and the adoption of calcium carbonate fillers therefore mark two major unintentional yet beneficial developments for permanence in paper history. The former was introduced in Europe to impart the characteristic translucence and "rattle" admired in parchment (Hills 1992), and the latter is compatible with alkaline papermaking and is cheaper, on a mass basis, than papermaking fibers. Between the 1980s and the present there has been a major shift from clay to calcium carbonate as the primary class of paper fillers, especially in the production of printing grades of paper, and this shift generally has had a beneficial effect on paper's storage characteristics (Sclawy and Williams 1981; McComb and Williams 1981; Wu and Tanaka 1998; Hubbe 2005).

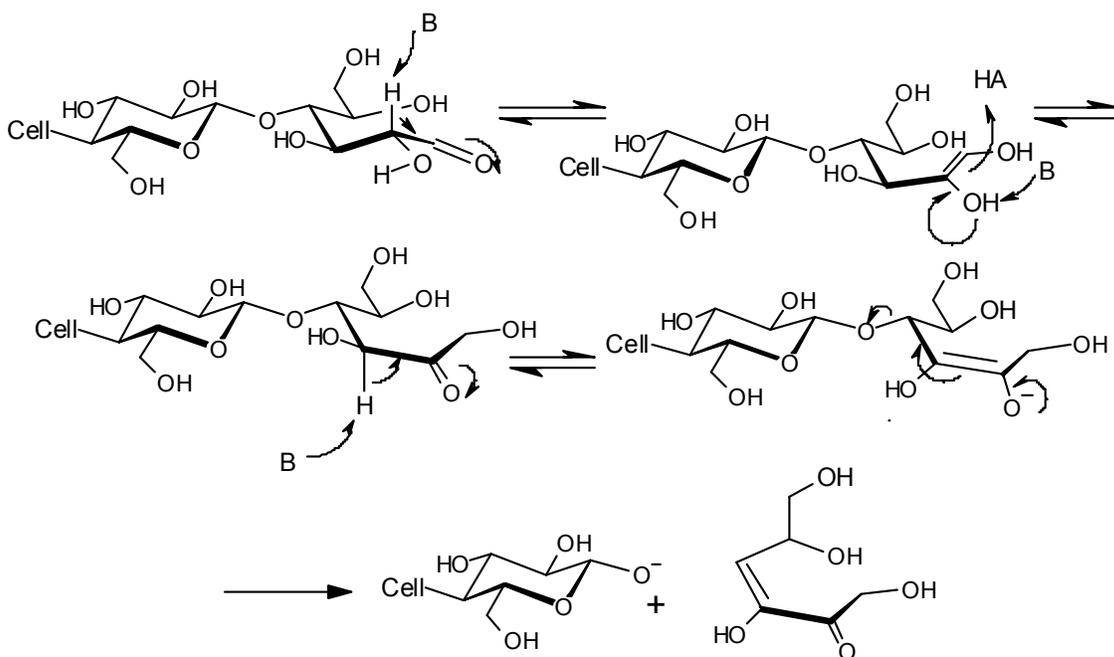
Excessive Alkalinity in the Presence of Oxygen

The alkaline pH of contemporary printing grades, which is often in the range of 7.5 to 9 due to the presence of CaCO₃ ($pK_a = 9.0$), generally has been regarded as favorable by conservation scientists. Considerable research effort *has* been expended, however, to ensure that deacidification, for the purpose of inhibiting the acid-catalyzed hydrolysis we describe below, will not inadvertently favor some other mechanisms of paper deterioration. Indeed, studies consistently show that there is potential for harm if pH conditions become excessively high, a factor that can depend on the type or amount of alkaline agent used to deacidify paper (Kolar 1997; Zappalà 1997; Malešič *et al.* 2002; Stefanis and Panayiotou 2007). What is less clear is whether librarians and curators need to be concerned. A decade-long series of research projects to address such concerns was carried out in Canada (Tse *et al.* 2002). The study found no evidence of problems related to "alkaline sensitivity" of deacidified paper under typical conditions of document storage.

Under sufficiently alkaline conditions the degradation of cellulose becomes significant. Under such conditions there are two 2-electron mechanisms that can cleave

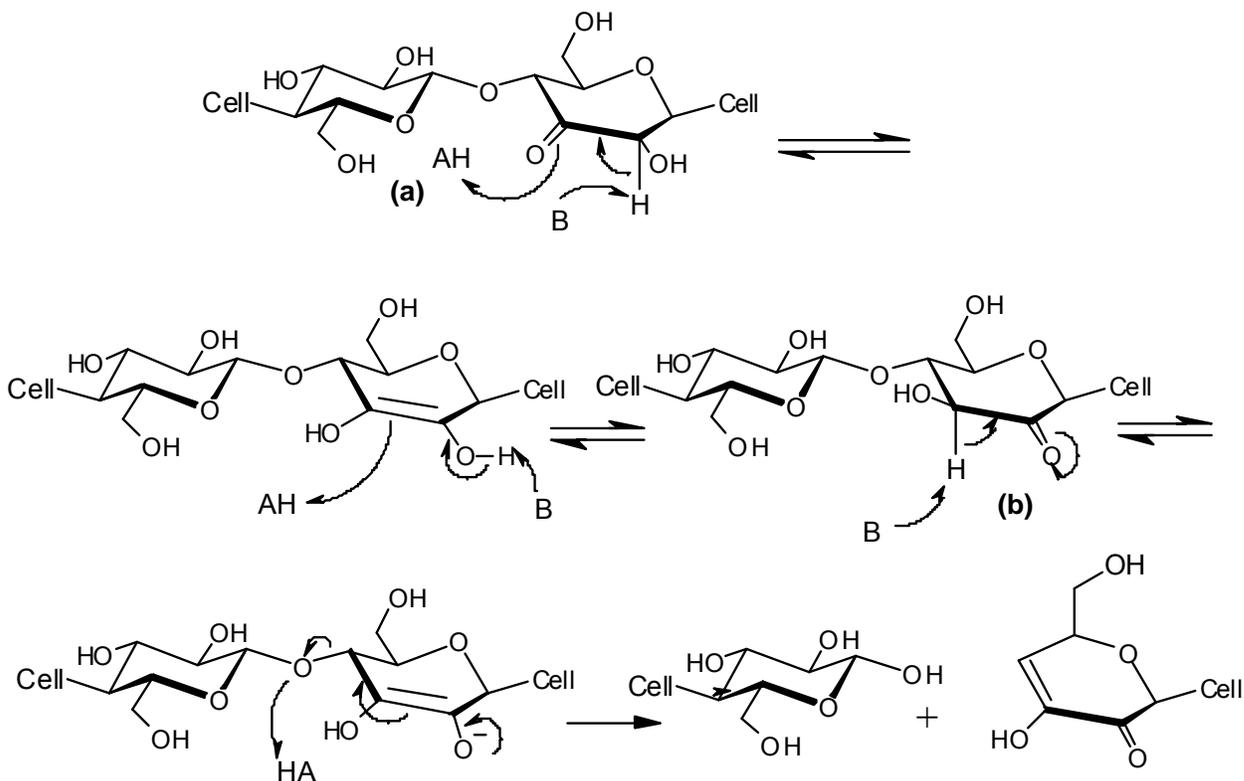
cellulose randomly, at any available glycosidic linkage. The most prominent mechanism described in the paper technology literature involves a nucleophilic substitution (Sjöström 1993). Brandon (1973) puts forward an alternative and perhaps complimentary pathway. Neither of these mechanisms is expected to proceed to a significant extent under ambient (*i.e.* library, museum, archival) conditions, as very high pH (14 and 12.3, respectively) and very high temperature ($>100^{\circ}\text{C}$) are required. Note that the first of the two reactions has sometimes incorrectly been called an “alkaline hydrolysis” (*e.g.* Dufour and Havermans 2001). The terminology has been reinforced by an erroneous caption in Sjöström’s wood chemistry text (1993), where it is apparent from looking at the mechanism that it is not a hydrolysis. The mechanism also reveals why *extremely* alkaline conditions are required for it to occur: the mechanism begins with the dissociation of the C2 hydroxyl, the pK_a of which is 14 (Nielsen and Sørensen 1983). To summarize, there is no “alkaline hydrolysis” of cellulose, and the mechanism incorrectly labeled as such is not relevant to library, museum, or archival conditions.

A third mechanism can cleave the cellulose endwise under alkaline conditions, meaning that it breaks off one anhydroglucose unit at a time from the reducing end. This mechanism, properly named β -alkoxy elimination, has earned the nickname “the peeling reaction” for this behavior (Scheme 1). The peeling reaction can be expected to occur in alkaline—indeed deacidified—papers to some degree. But two factors will reduce its significance to a minimum: (1) because the reaction proceeds endwise, the significance of each chain scission to any strength criterion will be much reduced; and (2) there exists a stopping reaction that can render the reducing end unavailable for further “peeling” (Sjöström 1993).



Scheme 1. β -alkoxy elimination, a.k.a. the “peeling reaction”

Though cellulose itself is stable under moderately alkaline conditions, oxidation reactions can be favored by increasing pH, depending on oxidizing species present in the system. Degradation due to oxidation under mildly alkaline conditions may be significant in the case of paper-based heritage collections (Daniels 1996; Kolar 1997; Bukovský 1999a, b, 2001; Polovka *et al.* 2006; Rychly *et al.* 2006). These ideas are consistent with a proposal by Arney and Jacobs (1979) that oxygen from the air plays a role in paper degradation and that oxidation reactions are promoted by higher pH (Arney *et al.* 1997; Arney and Novak 1982). Indeed, earlier tests showed that paper aging is faster in the presence of oxygen, compared to a nitrogen atmosphere (Major 1958; Parks and Herbert 1971). Reviewers have favored one-electron processes to explain alkaline-promoted oxidative cellulose chain scission in paper-based heritage collections, suggesting that the alkaline species particularly promote radical initiation (Kolar 1997). Note that chain scission may also result from a two-electron elimination mechanism beginning with the oxidation of either the C2 or C3 hydroxyls (Scheme 2). Although this mechanism resembles the peeling reaction discussed above, observe that it can occur at any point on the cellulose chain. Where the C2 is oxidized to a carbonyl, (b), the elimination is simple, but in the case of C3 carbonyls, (a), the elimination is preceded by keto-enol tautomerization.



Scheme 2. Cellulose chain scission resulting from oxidation. Either oxidation of the C3 hydroxyl to a carbonyl (a), or the same process on the C2 hydroxyl (b) can result in chain scission, but in the case of (a), the keto-enol tautomerization to (b) must occur first.

While oxidation of cellulose promotes alkaline degradation, it also promotes Brønsted-acid-catalyzed hydrolysis—the mechanism we describe in detail below. This promotion occurs principally via the oxidation of aldehydes such as aldoses to carboxylic acids. These acids catalyze further hydrolysis, exposing more aldehydes available for oxidation, and so on in a spiraling effect. This effect has come under investigation in the 1980s (Iversen 1989) and more recently with the work of Shahani and Harrison (2002). It is very likely that this spiraling effect is active in paper-based heritage collections to some degree. It is also the case that deacidification, which is designed “to knock out half of each loop” in the spiral, can be expected to be an effective means of stopping further decay via this scheme.

High Temperature

The rates at which chemical reactions proceed depend on a number of factors, including concentration, pressure, and temperature. Conservators and scientists take advantage of the observed temperature dependence of the rates of paper degradation, to both speed and slow paper's degradation. Obviously, the over-riding objective is to slow the rates of degradation in heritage collections, and this is the basis of cold storage policies (McCormick-Goodhart and Wilhelm 2004). Heating surrogate materials, speeding their degradation, makes it possible to compare different formulations and treatment conditions within a convenient period of time, an approach called *accelerated, artificial, or Arrhenius aging* (Rasch 1931; Gray 1969, 1977; Parks and Herbert 1971). Such aging studies have been used for many applications, including the aging of different paper samples under the same conditions so that one can infer which of them are more permanent. This is the basis for the ASTM accelerated aging test method (2002a). Such a comparison assumes that the temperature dependence of the efficient mechanism of degradation in both cases is the same, which is not necessarily the case. Calculating the temperature dependence of the degradation of paper-based heritage collections as a whole, however, is certainly a useful tool, enabling one to address the subject at hand, *i.e.* excessively warm long-term storage conditions as a factor affecting paper degradation. Here one can start with the rule of thumb of an approximate doubling of many chemical reactions for each 10°C that the temperature is increased. Specific to paper, Barrow (1963) found that an increase of 20°C in the aging temperature increased the rate of deterioration by a factor of 7.5. Michalski (2002) generalized for a variety of cultural heritage materials, including paper, that the life of such materials can be doubled with each five-degree drop in storage conditions. These calculations are considered in detail in a review article by Zervos and Moropoulou (2006).

Light

Light exposure can also induce significant changes in paper. Selli *et al.* (1998) showed that such processes can have a synergistic relationship with oxidation. Degradation of either carbohydrates or lignin was demonstrated, depending on the composition of the paper. It has been shown that oxygen consumption during exposure to light of paper that contained mechanical pulp was increased after deacidification treatments (Dufour and Havermans 1997; see Kolar *et al.* 1998). Likewise, it has been shown that photo-oxidation of lignin can cause significant yellowing (Bukovký 1997;

Dufour and Havermans 2001; Rychly *et al.* 2006). Fortunately, such susceptibility apparently can be reduced by treating the paper with a magnesium-containing compound, and it was proposed that the Mg was directly bound to the lignin, thus blocking the color-generating reaction (Bukovský and Kuka 2001). McGarry *et al.* (2004) showed that results of such tests can be highly dependent on the wavelength of the incident light. Robotti *et al.* (2007) investigated the effect of UV light. Dufour and Havermans' (2001) study of the photo-degradation of deacidified papers demonstrates an increased cleavage of the β -glycosidic bonds, rather than the expected oxidation of the C2 and C3 cellulosic ring carbons that is observed in the absence of alkaline species.

Biological Degradation

While libraries hold many fine examples of early paper with little sign of microbial attack, relatively little paper remains from the very distant past, back toward its invention (Hunter 1947), and it is likely that biological factors are partly to blame. We are therefore cautioned against a survivorship bias induced by beautifully-preserved extant specimens. Hunter (1947) proposed that many early paper documents were consumed by moths. Cunha and Cunha (1971) describe a variety of vermin and fungi that affect documents stored in libraries. Zerek (2006) compared various treatments to protect paper against mold damage. Finally, there is a danger that efforts to moderate the pH of paper may make it more attractive as food for some type of animal or plant. Rakotonirainy *et al.* (2008) describe measures to ward off fungal attack in papers that have been deacidified.

Hydrolysis

The Eponymous Factor—The Presence of Water

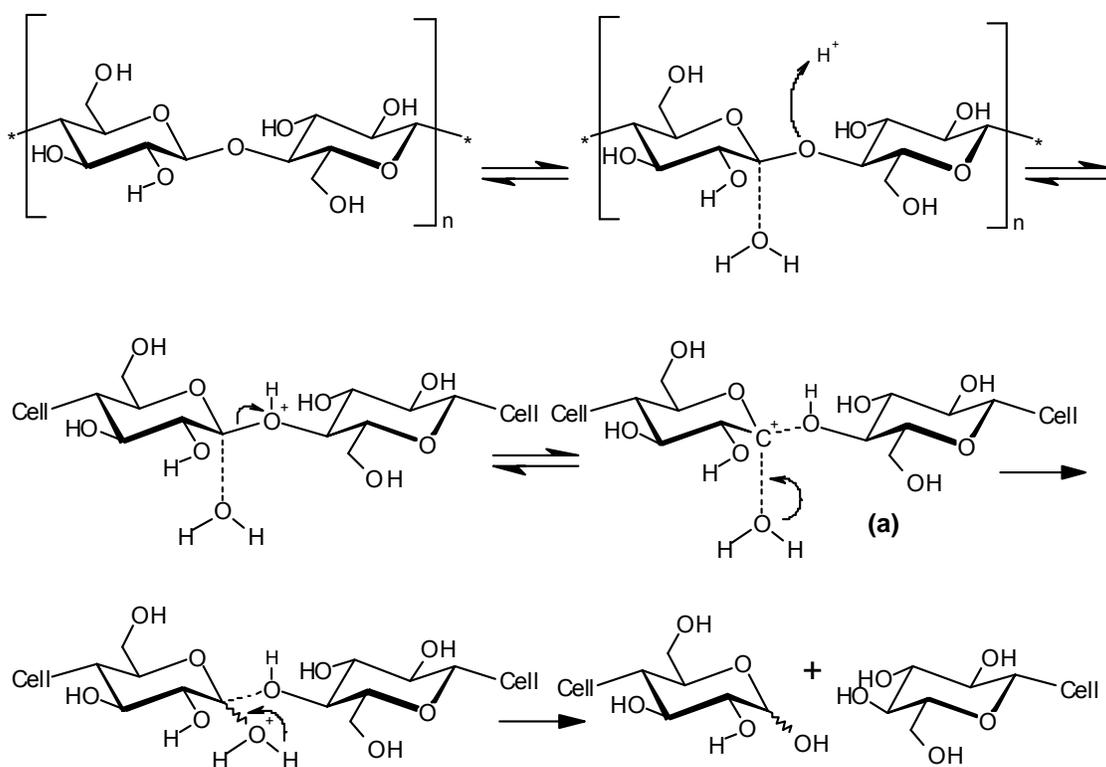
The hydrolysis of cellulose, as with any hydrolysis, cannot proceed without water. Under very dry conditions, however, in studies of purely cellulosic paper that is free from oxidizing agents besides oxygen (O₂), without species known to catalyze oxidation (such as transition metal ions), hydrolysis still appears to be the predominant mode of degradation over oxidation (Whitmore and Bogaard 1994, 1995). This generalization—that the amount of water vapor present is not the limiting factor in hydrolysis—cannot necessarily be extended to chemically complex systems. It is these complex systems that are of principal concern in paper-based heritage collections. Various studies of paper degradation have shown correlations between humidity and the rate of strength loss or reductions in cellulose degree of polymerization (DP) (Roberson 1976; Graminski *et al.* 1979; Du Plooy 1981; Welf *et al.* 2005; Zou *et al.* 1996a). Du Plooy (1981) showed a significant increase in the rate of paper degradation with increasing moisture content. Likewise Erhardt (1990) showed that the rate of glucose production, resulting from decomposition of polysaccharides in paper, increased with increasing moisture content during storage at elevated temperatures.

Catalysis

Until 1998 it was generally assumed that the hydrolysis of cellulose had to be catalyzed. In that year, however, Wolfenden and co-workers, using a small molecule to model cellulose, made some preliminary kinetics measurements of this spontaneous, *i.e.*

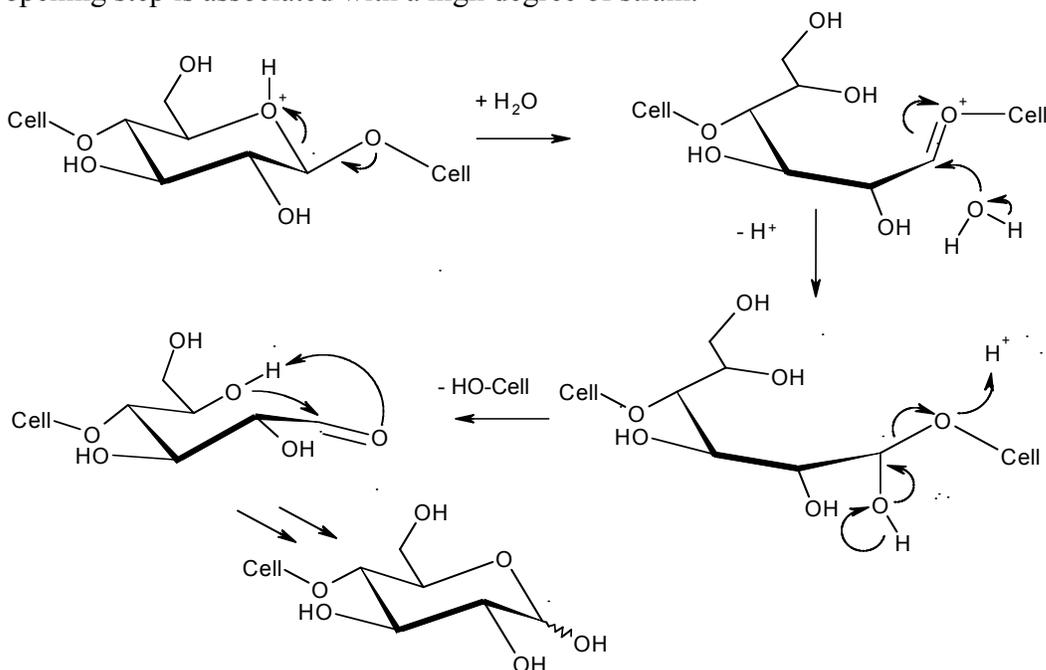
uncatalyzed process, and suggested that this degradation may be relevant to paper-based heritage collections in some cases. Baty and Sinnott (2005) greatly expanded that study using an improved model compound that effectively modeled cellulose around the glycosidic linkage for steric and inductive effects and concluded that, while the mechanism should be highly significant to alkaline pulping, the uncatalyzed process is too slow at ambient (library) conditions to do significant damage. Therefore, cellulose hydrolysis must be practically expected to proceed by a catalytic mechanism in paper-based heritage collections.

Conservation scientists have attributed the loss of strength of acidic paper to a Brønsted-acid-catalyzed hydrolysis of the cellulose, hereafter referred to as a *proton-catalyzed* hydrolysis of cellulose (Barrow 1963, 1967, 1974; Williams 1971; Arney and Novak 1982; Daniels 1996; Roth 2006). The prevailing mechanism for this degradation is given in Scheme 3. Incorporated into Scheme 3 is the critical observation that the glucopyranosyl cation cannot exist as a solvent-equilibrated intermediate, since its lifetime is less than the period of C-H or O-H bond stretching, and it therefore must be preassociated (Jencks 1981), in this case with water on C1, which is labeled (a) in the scheme. This mechanism has been thoroughly investigated with various leaving groups (Banait and Jencks 1991) and via kinetic isotope effect studies (Zhang *et al.* 1994); but the mechanism continues to be misrepresented in carbohydrate chemistry primers and review articles with schemes implying a solvent-equilibrated intermediate glucopyranosyl cation (Philipp *et al.* 1979; Sjöström 1993; Davis and Fairbanks 2002).



Scheme 3. Predominant mechanism of the proton-catalyzed hydrolysis of cellulose

An alternative mechanism for the proton-catalyzed hydrolysis of cellulose has been put forward in the cellulose technology literature (Philipp *et al.* 1979; Fan *et al.* 1987). The relative significance of the pathway shown in Scheme 4 has been demonstrated in other sugars, again via kinetic isotope effects (Bennet *et al.* 1985). A molecular modeling kit, however, shows a problem immediately for the six-membered rings in cellulose: Pyranoses readily assume the 4C_1 (chair) conformation, and the ring-opening step is associated with a high degree of strain.



Scheme 4. Proton-catalyzed hydrolysis of cellulose proceeding from the protonation of the ring oxygen and involving ring opening

The significance of the proton-catalyzed process in the conservation science literature is the continuously affirmed connection between acidity, variously measured, and the rate at which paper loses its strength during storage or during accelerated aging tests (Roberson 1976; Koura and Krause 1978; Arney and Chapdelaine 1981; Arney and Novak 1982; Eggle *et al.* 1984; Kolar *et al.* 1998). Acidity can be quantified by measuring either the pH or the concentration of bound weak acid groups.

Aluminum sulfate, often called “papermaker’s alum,” can be considered a major source of both Brønsted and Lewis acidity in many of the books and documents that are of greatest concern. The role of aluminum sulfate in papermaking, as well as its increased use after 1807 in combination with rosin for the hydrophobic sizing of paper has been previously reviewed (Wilson and Parks 1979; Barrett 1989; Gurnagul *et al.* 1993; El-Saied *et al.* 1998; Baty and Sinnott 2005). We elaborate on its peculiar role in paper degradation below.

Air pollution has also been identified as a key contributor to the degradation of books and paper (Daniel *et al.* 1990; Daniels 1996; Havermans *et al.* 1995; Bégin *et al.*

1999; Dupont *et al.* 2002). Sources of acidity include airborne sulfur, *i.e.* the components of smog and acid rain. An observed rapid deterioration of books stored in some urban settings, compared to similar books in other libraries, has been attributed to differing levels of acidic gases such as SO₂ in the atmosphere. Accordingly, an ASTM test has been established to evaluate the “accelerated pollutant aging” of paper exposed to standard atmospheric conditions (ASTM 2002c).

A number of additional sources of acidity in paper have been identified (Barański *et al.* 2005; Gurnagul *et al.* 1993; Leschinsky *et al.* 2009; Zervos 2010). Among the most prominent of these come from hydrolysis of ester functionalities in the fibers as, for example, from the acetate substitution of certain important hemicelluloses, releasing acetic acid (Barański *et al.* 2005).

Leaving aside protons for a moment, other catalysts of cellulose hydrolysis in paper degradation include enzymes and the electrophilic metal ion aluminum(III). Enzymes will catalyze paper degradation, though only with the involvement of the organisms that produce them, and this subject is therefore really biological rather than chemical degradation. But occasionally enzymes can teach us something about mechanisms by which other catalysts can affect cellulose hydrolysis. For example, the *LacZ* β-galactosidase enzyme of *Escherichia coli* has a magnesium(II) ion in its active site. This metal center is not required for catalytic activity, but when present, it has been shown to accelerate glycoside hydrolysis, and the balance of evidence suggests that the ion is acting as an electrophile (Sinnott 1990). Given the extensive use of magnesium(II) in deacidification—comprehensively described below—it is important to ensure that it does not itself catalyze cellulose hydrolysis in paper. Substantial anecdotal evidence from evaluating deacidification methods via accelerated aging suggests that magnesium(II), as well as other alkaline earth cations, are benign agents in that way, and preliminary tests rigorously controlling for the behavior of this cation are also encouraging (Baty *et al.* 2010).

Aluminum(III), the metal center having the shortest atomic radius, is a known catalyst for cellulose hydrolysis. Aluminum salts were likely first introduced to paper when added to limit the putrefaction of gelatin sizing, as well as to harden it (Brückle 1993). They gained widespread use in the earliest major internal—“rosin-alum”—sizing (Hunter 1947) and continue to be used as flocculation, drainage, and retention aids, to fix resins and dyestuffs, and for pH control (Scott 1996). An Al^{III} electrophile-catalyzed hydrolysis of cellulose was first discussed tangentially in the cellulose technology literature twenty years ago (Popoola 1991; Sarybaeva *et al.* 1991), followed by a targeted molecular model study (Baty and Sinnott 2005), and subsequently by discussion in the paper technology literature (Chamberlain 2007). Still, as of this writing electrophilic catalysis remains untested for its real relevance to paper degradation of actual paper-based heritage collections. This lack is significant in the conservation science literature, particularly in the context of deacidification, where aluminum salts are generally regarded merely as a source of protons for the proton-catalyzed process described above.

Paper pH Evaluation

With these alternative catalysis mechanisms of cellulose hydrolysis in mind, we return to the significant mechanism of catalysis by protons. To evaluate this mechanism

it is desirable to have a precise and accurate measure of the proton concentration—"the pH"—of paper (Kohler and Hall 1929). As noted above, "paper pH" may not be rigorous in terms of solution theory, but it is an established and useful concept, deriving primarily from the pH of paper extracts, measured via the hot or cold extraction method of 1 g of paper in 70 mL, as defined by TAPPI (2002a, b). An extract containing macerated fibers can be achieved by cutting up the paper sample and redispersing the fibers in deionized water, usually with the help of intense mechanical agitation. Alternatively, the paper may be extracted, using a reflux condenser. These methods are destructive, however, and therefore a surface pH measurement, also defined by TAPPI (2002c), is preferred by conservators. Here, a drop of deionized water or neutral salt solution is placed on the paper surface, and after a suitable time of equilibration, the pH is measured with a specially designed "flat" electrode (Anon 1995b; Anguera 1996; Joel *et al.* 1972; Kolar and Novak 1996). Testing strips for pH, available from Merck Chemicals and other vendors, are also employed. One should recall that a "paper pH" criterion is a snapshot of the concentration of protons at any particular time and will not indicate how much of a strong acid or base is needed in order to change the pH to a desired value. That is, pH measurements cannot predict the pK_a s of weak acids or bases present within the sheet, nor their concentration. Titrations are needed in order to obtain the latter information (Graminski *et al.* 1979; Kelley 1989; Kaminska and Burgess 1994; Stroud 1994; Liers 1999; Bukovský 2005; Ipert *et al.* 2005).

DEACIDIFICATION AGENTS

Although deacidification agents include strong bases such as NaOH, the materials most often used for deacidification are weak bases, including carbonates, bicarbonates, some hydroxides, various oxides, as well as amines (Cunha 1987). Cedzova *et al.* (2006) have listed a large number of such materials that have been claimed in different patents. By patent date these agents include the alkaline earth carbonates or hydroxides (1936), barium hydroxide (1969), alkaline oxides (1972) gaseous hexamethylenetetramine (1972), gaseous morpholine (1973), methyl magnesium carbonate (1976), diethyl zinc (1976), magnesium(II) oxide (1982), zinc carbonate, sodium carbonate (1988), amine compounds (1989), ammonia (1989), carbonated ethoxymagnesium-methoxypolyethoxide (1992), organic aluminum carbonate (1993), ethyl magnesium carbonate (1993), dibutylmagnesium (1993), tetrabutyl titanium (1994), and alkoxides of alkaline earths (1997).

Carbonates

The alkaline earth carbonates, namely calcium carbonate (CaCO_3) and magnesium carbonate (MgCO_3), must be considered as leading candidates for deacidification in light of their chemical simplicity, relatively low cost, high brightness, and suitability for use as paper fillers (Arney *et al.* 1979; Kundrot 1985; Kolar and Novak 1996; Giorgi *et al.* 2002; Botti *et al.* 2005). Barrow (1965) used aqueous suspensions of these materials in his early studies of deacidification. Brederick *et al.* (1990) reported favorable results when using dolomite ($\text{CaMg}(\text{CO}_3)_2$) for deacidification. Simple carbonates, however,

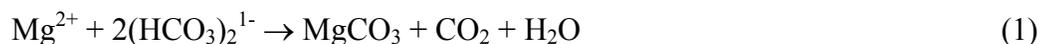
tend to be relatively insoluble in neutral water, as well as in organic solvents, a factor that limits their manner of distribution in paper-based documents (see below for bicarbonate solutions.)

Kolar (1997) noted that MgCO_3 imparts a higher pH than CaCO_3 . Santucci (1973-4) observed cases in which Mg compounds caused accelerated aging of pure cellulose paper, whereas calcium carbonate did not. It is known, however, that some precipitated CaCO_3 products contain some residual calcium hydroxide (Ca(OH)_2), such that when they are equilibrated with water the pH can rise well above 9 (Brown 1998). By contrast, relatively pure calcium carbonate products, as well as essentially all limestone and chalk products, tend to buffer the pH in a more moderate range of about 7.5 to 8.5 (Brown 1998; Wu and Tanaka 1998).

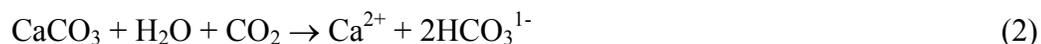
Compounds such as magnesium methylcarbonate and methyl-methoxymagnesium carbonate have been used as solvent-soluble carbonates (Kelly 1976; Kelly *et al.* 1977; Morrow 1988; Lienardy and van Damme 1990). Cyclohexylamine carbonate has also been used in such non-aqueous applications (McCarthy 1969; Cunha 1987), though the toxicity of this system has been criticized (Williams 1971).

Bicarbonates

Bicarbonates of alkaline earth metals, in general, are expected to have greater solubility in water, compared to the corresponding carbonates, a difference that can aid in their distribution when used for deacidification. For example, MgCO_3 is considered practically insoluble in water (106 mg/L at room temperature); this increases to moderate solubility under a partial pressure of carbon dioxide (350-590mg/L with a corresponding partial pressure of 2-10 atm CO_2), where magnesium bicarbonate ($\text{Mg(HCO}_3)_2$) is formed in solution. Upon evaporation of water, or removal of $\text{CO}_2(\text{g})$, magnesium carbonate is precipitated (Patnaik 2003):



Similarly, CaCO_3 is insoluble in water (15mg/L at room temperature), but dissolves in the presence of CO_2 with the formation of bicarbonate (Patnaik 2003):



Despite its increased solubility relative to CaCO_3 , $\text{Ca(HCO}_3)_2$ remains ten times less soluble than $\text{Mg(HCO}_3)_2$ (Daniels 1987).

Neither $\text{Mg(HCO}_3)_2$ nor $\text{Ca(HCO}_3)_2$ exist as solid crystals; upon drying it is the corresponding carbonate that is deposited in the paper fibers. As bubbling with CO_2 is a necessary part of preparing these aqueous bicarbonate solutions, the pH of these solutions is somewhat decreased by the formation of carbonic acid (H_2CO_3) as a result of the reaction of water and CO_2 (Daniels 1987).

Various studies have examined the efficacy of bicarbonate deacidification treatments; the results of these studies are summarized in Table 3.

Table 3. Studies of Alkaline Earth Bicarbonate Deacidification Treatments

References	Alkaline Agents Studied	Observations, Results, and Conclusions
Wilson <i>et al.</i> 1981	bicarbonate solutions	1. Beneficial effects on the stability of paper strength and brightness following treatment. 2. Loss of hydrophobic nature of the paper in old maps and other old paper samples
Lienardy and van Damme 1990	Ca(OH) ₂ Ca(HCO ₃) ₂ Mg(HCO ₃) ₂ Borax (Na ₂ B ₄ O ₇ ·10H ₂ O) various non-aqueous agents	1. Reject NaHCO ₃ as a treatment option due to observed shrinking of paper and changes in inks and colorants. 2. Provide recipes for preparation of deacidification agents. 3. Test treatments on rag, chemical pulp and wood pulp papers. 4. Conclude Ca(HCO ₃) ₂ leaves insufficient alkaline reserve. 5. Mg(HCO ₃) ₂ results in yellowing of treated papers
Bredereck <i>et al.</i> 1990	Ca(OH) ₂ Ca(HCO ₃) ₂ Mg(HCO ₃) ₂ Ca(HCO ₃) ₂ + Mg(HCO ₃) ₂	1. Either Mg(HCO ₃) ₂ or Ca(HCO ₃) ₂ + Mg(HCO ₃) ₂ mixture chosen as most suitable system
Anguera 1996	Ca(OH) ₂ Ca(HCO ₃) ₂ Mg(HCO ₃) ₂ Ca(HCO ₃) ₂ + Mg(HCO ₃) ₂	1. Milder Ca(HCO ₃) ₂ + Mg(HCO ₃) ₂ treatment yielded greater improvements in permanence than Ca(OH) ₂
Bansa 1998	Ca(HCO ₃) ₂ Mg(HCO ₃) ₂	1. Mg(HCO ₃) ₂ treatments display improvements relative to untreated control, but show a greater degree of yellowing, greater decrease in brightness, decreased strength and decreased degree of polymerization relative to Ca(HCO ₃) ₂ . 2. Greater alkaline reserve left by Mg(HCO ₃) ₂

Several studies on bleached chemical pulp model papers (Kolar *et al.* 1998; Reissland 2001; Bansa 1998; Kolar and Novak 1996) revealed increased degradation and discoloration due to treatment with Mg(HCO₃)₂. Malešič *et al.* (2002) attribute this to the high pH and high carbonyl-group content of these papers, resulting in an increased oxidative decay. Reissland (2001) also notes that the colored complex of iron gall ink is unstable above pH 8.5, making deacidification with Mg(HCO₃)₂ a poor choice in such cases.

Hydroxides

Though various metal hydroxides provide very effective treatment of excess acidity, they tend to yield pH values significantly higher than neutral. Most of the related work has involved calcium hydroxide (Ca(OH)₂) (Williams 1971; Hey 1979; Kolar and Novak 1996), though the use of barium hydroxide (Ba(OH)₂) has also been used as an alkaline agent, primarily in non-aqueous deacidification (Baynes-Cope 1969; Lienardy and van Damme 1990). Indeed, it is reported that the British Museum had used Ba(OH)₂ for deacidification as early as 1890 (Cunha 1987), with the primary disadvantage that the barium hydroxide solute is toxic. Hey (1979) employed a saturated aqueous solution of Ca(OH)₂ diluted 1:1 with deionized water to prevent the aforementioned CaCO₃ precipitation from occurring at the bath stage before the calcium hydroxide has

penetrated into the fiber network, resulting in surface deposition of insoluble CaCO_3 . Giorgi *et al.* (2002) noted that once Ca(OH)_2 particles are deposited in paper, they have the theoretical capability of reacting with carbon dioxide from the air, thus forming calcium carbonate *in-situ*. Several authors (Guerra *et al.* 1995; Sundholm and Tahvanainen 2003a, 2004) report effective use of an aqueous Ca(OH)_2 suspension in combination with a strengthening agent such as methyl cellulose.

Due to concerns about both aqueous and non-aqueous solubility of alkaline earth hydroxides, recent investigations have centered on the use of very finely divided suspensions, *i.e.* “nanoparticles”. Both aqueous and non-aqueous (*e.g.* isopropanol) suspensions of nanoparticle dispersions of Ca(OH)_2 have been reported as effective deacidification agents (Giorgi *et al.* 2002), including their use of items inscribed with iron gall ink (Sequeira *et al.* 2006). Giorgi *et al.* (2005) synthesized magnesium hydroxide (Mg(OH)_2) nanoparticles and evaluated their use in paper conservation. Stefanis and Panayiotou (2007) deacidified paper with micro- and nano-particulate dispersions of Ca(OH)_2 or Mg(OH)_2 and reported evidence of cellulose breakdown when unaged paper was treated; these adverse effects were attributed to excessively high pH.

Metal Oxides

In principle, many metal oxides are easily converted to their corresponding hydroxide or carbonate forms by their interactions with water or carbon dioxide, respectively. For instance, calcium(II) oxide (CaO , also called burnt lime) can be “slaked” by the addition of water, forming Ca(OH)_2 , and the “slaked lime” thus formed can further react with carbon dioxide to form CaCO_3 . The latter materials already have been mentioned here as among the more promising alkaline agents for deacidification or to serve as an alkaline reserve in the deacidified paper. Unfortunately alkaline earth oxides are only sparingly soluble in aqueous and non-aqueous media. In this respect it makes sense that the Bookkeeper® process initially developed by Koppers employs submicrometer particles of magnesium and calcium oxides (Cunha 1987, 1989). In use, these are expected to be converted to the hydroxide form and possibly even to the carbonate form.

Sodium Tetraborate (Borax)

The use of sodium tetraborate (borax) also has been reported for deacidification of paper (Daniel *et al.* 1990; Lienardy and van Damme 1990; Basta 2004; Botti *et al.* 2006). Borax is widely used as an alkaline buffer in such applications as laundry detergents. Botti *et al.* (2006) note that borax is convenient to use and serves as a mild fungicide, but also remark that some researchers have concerns about negative side effects, such as a sharp decrease in DP of the cellulose, as well as pronounced yellowing of the paper after moist heat accelerated aging. Lienardy and van Damme (1990) specifically reject the use of borax as a deacidification agent, due to a decrease in DP after humid aging, particularly in the presence of iron, an observed change in inks and pigments, and a total and immediate loss of strength in wood pulp paper upon aging. By contrast, after borax treatment and accelerated aging, rag papers are found to maintain acceptable pH levels, adequate alkaline reserve, while also displaying sound mechanical properties.

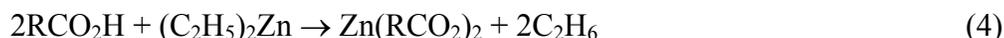
Amines

Various amine compounds also have been considered as alkaline agents suitable for paper deacidification. These include ammonia (Kathpalia 1973; Koura and Krause 1980), hexamethylenetetramine (Kuster and Hind 1972), morpholine (Kusterer and Sproull 1973; Walker 1977; Cunha 1987), ethanolamine (Yoon *et al.* 2008), and aminosilanes (Cheradame *et al.* 2003; Rousset *et al.* 2004; Ipert *et al.* 2005, 2006; Rakotonirainy *et al.* 2008). Ammonia is noted to have only temporary deacidification effects due to its volatility under standard atmospheric conditions (Cheradame *et al.* 2003). In an attempt to develop a mass deacidification treatment not dependent on a magnesium-containing compound, Rousset *et al.* (2004) report greater success with liquid phase aminosilanes, than those found by Cheradame *et al.* (2003) with gas phase aminosilanes. Yoon *et al.* (2008) note that ethanolamine, in addition to providing alkalinity, also tends to scavenge metals such as Al^{III}, Cu^{II}, and Fe^{III}, which otherwise can accelerate paper's decomposition.

Alkyl Metal

A number of alkyl metal compounds have been used in non-aqueous deacidification treatments. The most widely used has been diethyl zinc ((C₂H₅)₂Zn or DEZ), which can be applied as a vapor using specialized equipment (Smith 1987; Sparks 1987; Hon 1989; Schwerdt 1989; MacInnes and Barron 1992; McCrady 1992; Yamazaki *et al.* 1992; Kaminska and Burgess 1994; Lienardy 1994; Stroud 1994; Havermans *et al.* 1995). The compound is understood to react with water vapor in the paper, yielding an insoluble deposit of zinc(II) oxide (ZnO), an alkaline material.

Key steps in the DEZ process involve the reaction of the (C₂H₅)₂Zn with either water or acidity in the sheet, as represented by the following equations (Cunha 1987),



where "R" represents part of the cellulosic material that is bound to a carboxylic acid group.

A number of other non-aqueous alkyl metal compounds have been investigated. Kamienski and Wedinger (1994) showed that various metal alkoxy alkoxides were able to react with gaseous carbon dioxide after being deposited into paper, thus forming CaCO₃ *in-situ*. MacInnes and Barron (1992) found that magnesium butoxytriglycolate (MG-3), the deacidification agent used in the FMC or Lithco process, was inferior to DEZ with respect to uniform distribution in the paper.

Metal Alkoxides

Methoxymagnesium methylcarbonate (MMMC), H₃COMgOCOOCH₃, is the deacidifying agent presently used by practitioners of the Wei T'o process. In principle, this reagent is able to react with residual moisture in the paper according to the following scheme (Cunha 1987):



Acidity in the paper, as represented by carbonic acid, then can react with the magnesium hydroxide as follows, forming magnesium carbonate,



which already has been mentioned as a possible deacidifying agent and potential contributor to the alkaline reserve within paper. In practice, the Wei T'o process involves a mixture of alkaline agents deposited in the paper, including $\text{MgO} \cdot \text{MgCO}_3 \cdot \text{Mg(OH)}_2$, MgO , MgCO_3 , and Mg(OH)_2 (Cunha 1987).

Magnesium titanium alkoxide has been used as a deacidifying agent in the Papersave® process, as practiced by the Battelle Institute (Banik 2005). A process using this agent was judged to be one of the most effective, among the agents evaluated in the cited study. Calcium and magnesium alkoxides, in conjunction with quaternary ammonium bromide antioxidants are being developed for the Inksave® process. This process is a modified Papersave® process, designed specifically for the stabilization of iron gall ink containing materials (Lichtblau and Anders 2006; Reissland *et al.* 2006; Kolar *et al.* 2006). Both a non-polar suspension and a polar solution variation of Inksave® are being developed.

Antioxidants and Reducing Agents

While antioxidants and reducing agents are not alkaline, their use can be closely linked to certain deacidification schemes. For instance, calcium phytate is a chelating agent that is used to protect cellulose from iron(II)-catalyzed degradation, primarily for iron gall ink containing documents, a use for which it has demonstrated substantial benefits (Neevel 1995; Kolar and Strlič 2004; Botti *et al.* 2005; Hansen 2005; Kolar *et al.* 2005; Zappalà and De Stefani 2005; Havlinova *et al.* 2007; Henniges and Potthast 2008). Figure 3 shows an example of the damage that can be caused by this Brønsted-acidic and oxidation-catalyzing type of ink. Calcium phytate treatment is generally paired with calcium bicarbonate deacidification, as this deacidification method does not raise the pH above 8.5, the point at which iron gall ink colorants begin to break down (Kolar *et al.* 1998).

Analogously, it has been found that iodide can function as a protective agent when cellulosic material is subjected to humid, hot conditions during accelerated aging (Williams *et al.* 1977) or when paper containing ZnO is exposed to sun-lamp irradiation (Kelly and Williams 1981). Halides are known to act as antioxidants that retard Fenton-like reactions involving transition metal catalysis. Malešič *et al.* (2005a,b) experimented with a number of different quaternary ammonium bromides, quaternary phosphonium bromides, alkali bromides, and quaternary ammonium chlorides, finding that the antioxidant properties of the halides were relative to the size of the associated cation. Halides with large cations, such as tetrabutyl ammonium bromide and alkyylimidazolium bromides have received attention as possible antioxidants for use in book and paper conservation (Kolar *et al.* 2008; Maitland 2009).

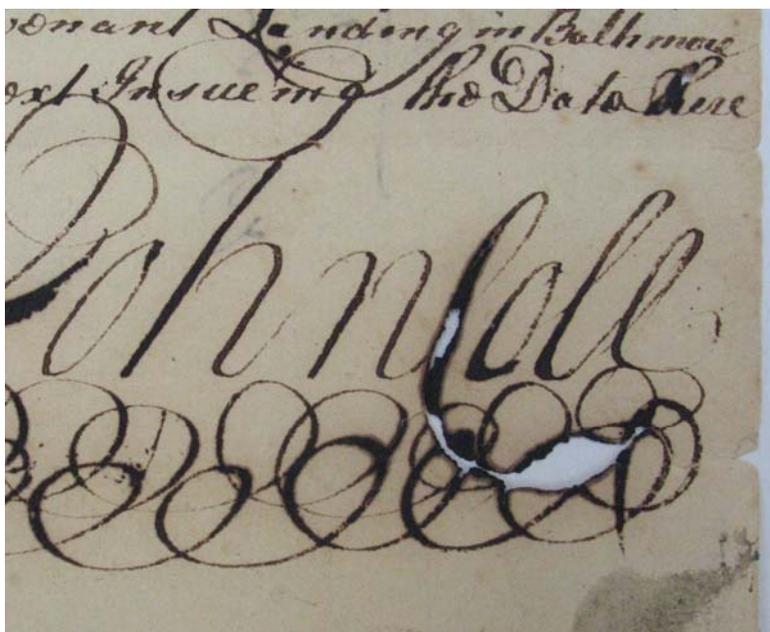


Figure 3. Example of paper that has been degraded by the combined acidic and oxidative nature of the applied iron gall ink

A more aggressive approach, beyond the use of antioxidants, involves chemical modification of deacidified paper to remove chemically vulnerable sites. For instance, the paper can be treated with a reducing agent such as sodium borohydride (NaBH_4) or potassium iodide (KI) (Kolar *et al.* 1998; Tang 1986). The first cited authors noted that while some aldehyde-containing substances can be removed from paper during aqueous deacidification, such compounds remain in paper that has been deacidified under non-aqueous conditions, thus providing a point of vulnerability to oxidation. If these aldehydes can be reduced to alcohol functionalities, they become less targeted as oxidation sites. Tang notes that while NaBH_4 can be shown to stabilize paper and increase its brightness, this moderately strong reducing agent can have negative effects on media and must be used with care. Bogaard and Whitmore (2001) found that photo-oxidized paper could be effectively stabilized against accelerated aging by chemical reduction, followed by washing with dilute alkaline calcium solution.

DISTRIBUTION METHODS

The most critical step in any deacidification treatment involves distribution of an alkaline agent uniformly within the treated books or other paper-based items, with a minimum of damage, with acceptable cost, and with the greatest practical degree of convenience. Due to the importance of this subject, a number of previous authors have provided general discussions of methods by which alkaline agents are distributed into various paper-based items (Couch *et al.* 1985; Cunha 1987; Albrecht and Turkovics 1991; Carter 1996b; Reissland 1999; Cedzova *et al.* 2006; Lichtblau and Anders 2006).

Aqueous Treatments

Among the fluid-based deacidification schemes considered, aqueous treatments were the earliest to be developed (Schierholtz 1936; Barrow 1965; Anon. 1968; Kelly and Fowler 1978; Ramarao and Kumar 1986). Wash temperatures, alkaline solutions, and drying methods have been optimized (Hey 1979; Bredereck *et al.* 1990; Daniel *et al.* 1990; Shaw 1996; Bansa 1998; Sundholm and Tahvanainen 2003a-b, 2004). Aqueous treatments also have been carried out as a reference point during the evaluation of non-aqueous treatments (Green and Leese 1991). Aqueous treatments are preferred by conservators for bench-scale deacidification of single items, but often they require that the book be disbound and pages washed, deacidified, resized, and then rebound—a laborious process that is reserved for paper conservators having the equipment and technical expertise to complete the treatment and the binding (Barrow 1963; Williams 1981).

Barrow first immersed paper in a saturated solution of $\text{Ca}(\text{OH})_2$, followed by immersion in a $\text{Ca}(\text{HCO}_3)_2$ solution (Barrow 1965; Anon. 1976). This two-bath technique also was adapted for spray treatment of acidic papers (Moll 1965). One of the potential advantages of aqueous treatments is that washing and deacidification of the paper can be carried out in the same operation (Tang 1981; Lee *et al.* 2006). For instance, Lee *et al.* (2006) recommends that alkaline water be used for washing. Hey (1979) takes it further, calling for alkaline washing followed by deacidification; the first step neutralizes the existing acids in the paper, whereas the second step deposits an alkaline reserve. Table 4, at the end of this section, summarizes the various applications of aqueous alkaline agents. The low solubility of many of the alkaline agents in water remains an obstacle to introducing sufficient alkaline reserve (Kelly 1972).

Aqueous treatments generally offer an advantage over other deacidification strategies insofar as they make it possible to make soluble and remove organic acids from the document. A study reported by Tse *et al.* (2002) confirmed the beneficial effects of aqueous washing. The study showed that the overall effect of washing was beneficial even in cases where there was a detectable decrease in the amount of alkaline reserve. Moropoulou and Zervos (2003), on the other hand, demonstrate that aqueous treatments can weaken the paper structure, despite the fact that the alkaline condition renders the cellulose resistant to further degradation. This observation is not necessarily borne out in the experience of conservators, who find that paper emerges from aqueous treatments with increased strength properties; the study authors suggested that uneven drying and the resulting stresses generated within the paper might be responsible for lower strength. An additional likely explanation is that after the swelling and opening of hydrogen bonding between fibers during the wetting process, upon re-drying the paper has a lower apparent density than was achieved in the paper mill, where higher pressing pressures may have been used before and during the initial drying. Removal of paper size and other components during aqueous methods could also explain the observed decrease in strength.

Kelly and Fowler (1978) compared different strategies to achieve prompt and uniform permeation of aqueous solutions into paper, while carrying a variety of alkaline agents. They found that an addition of 10% ethanol was effective. It is well known that ethanol reduces the surface tension of water, thus reducing capillary forces that can resist

wetting. Hey (1979) concurs, stating that proper wetting of paper is essential to maximize benefits of washing and deacidification treatments. Hey goes into detail about the length of bath time, the swelling of fibers, and the options for pre-wetting with alcohols. To avoid migration of salts during drying, it was found that marginally better results could be achieved with freeze drying when compared to ambient air drying (Kelly and Fowler 1978). The same authors also developed a novel double-decomposition technique to precipitate calcium carbonate in a relatively uniform manner throughout the sheet by simultaneously introducing calcium chloride and ammonium carbonate solutions from opposite sides of a sheet of paper, but such lengths are rarely practiced by conservators.

Barrow also experimented with the aqueous treatment of intact textblocks in the 1960s, where the book covers had been removed, but the sewing remained intact (Cunha 1987). The books were immersed in aqueous suspensions of $\text{Ca}(\text{OH})_2$ and CaCO_3 . The pages were badly distorted during drying following this process, and the approach became less used for many years. However, essential features of the approach have been revived more recently in what has become known as “washing intact and air drying” (Minter 2002). The bound book is immersion-washed and deacidified, and then dried with an absorbent material interleaved throughout and extending beyond the textblock. Drying was done inside a wind tunnel with the textblock under a moderate weight, minimizing any paper distortion.

Combined Aqueous Deacidification and Strengthening

One considerable advantage of aqueous-based treatment systems is that they are compatible with traditional means of strengthening paper by impregnation with sizing agents (Cunha 1989; Porck 1996). External sizing imparts a connectivity of the fibers to one another, improving handling and most importantly, serving as a barrier to hygroscopicity of paper. Starch was originally used in hand-made Arabic papers, along with burnishing the surface (Bloom 2001; Hubbe and Bowden 2009). In the West, external sizing has used a variety of protein-based gelatin adhesives, including skin and bone from a variety of sources (Kern 1980; Turner and Skiöld 1983). Today, while this protein sizing is still used, better and purer gelatin is available. To combine strengthening and deacidification, cellulose derivatives are often selected, because of their chemical similarity to cellulose. Sonoda *et al.* (2009) demonstrate that cellulose derivatives soluble in water, such as methyl cellulose (MC) and carboxymethyl cellulose (CMC), added to distilled water of 80°C with MgCO_3 carbonate dispersed in alcohol proved to have both deacidification and strengthening qualities. Guerra *et al.* (1995) and Sundholm and Tahvanainen (2003a, 2004) showed benefits of treating paper with a mixture of $\text{Ca}(\text{OH})_2$ and MC. The latter additive functions as a dry-strength agent, tending to increase the amount of hydrogen bonding between adjacent fibers (Hubbe 2006). In addition, the MC likely helps to keep the particles of deacidification agents well dispersed, aiding in their even distribution. Basta (2004) showed that paper could be strengthened by immersing it in an aqueous solution of polyvinyl alcohol in combination with borax as an alkaline buffering agent. Hanus (1994) recommends sizing the paper with an aqueous mixture of CMC and gelatin.

New combined processes have been based on aminoalkylalkoxysilanes (AAAS), which have low solubility parameters and incorporate some paper strengthening properties. Using such agents for deacidification results not only in deposition of alkaline reserve, based on the amino functionalities, but also in improved folding endurance. The reason for this effect is not yet established, but there is evidence to suggest that the cellulosic fiber is strengthened by an interpenetrating polymer network (Cheradame 2009).

The Vienna process

A mechanized process, named for the location where the technology was developed (Wächter 1987; Porck 1996; Lienardy and van Damme 1990; Anon. 1999a), the Vienna process is usually performed on unbound newspapers, which are then bound after treatment. Materials are immersed in aqueous suspensions of alkaline agents and strengthening agents, such as $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{HCO}_3)_2$, and bicarbonate, which are mixed with a strengthening agent such as MC, followed by freeze-drying at -30 to -40°C to remove the water and to prevent pages from cockling in the drying process. The Vienna process has been used since 1987 by the Austrian National Library. Brederick *et al.* (1990) noted that the amount of alkaline agent deposited when using the Vienna process tended to be relatively low, in the range zero to 0.7% in their study, but otherwise the results were satisfactory. The MC used in the process is said to increase the paper strength by 150% (Carter 1996b). Porck (1996) mentions that the Viennese process may have employed polyvinyl acetate as a co-strengthening agent with MC; this resulted in a four-fold increase in folding endurance after treatment.

Bückerburg conservation procedure, Neschen AG, and the C-900

This three-component aqueous system, used in both German and Polish libraries since 1995, acts as a combined deacidification and strengthening mass treatment for single-sheet materials. The technique was initially investigated by the State Archives in Bückerburg, Germany, starting in the 1970s. Development was adopted by Neschen AG in 1996 (Porck 1996). The aqueous treatment solution contains $\text{Mg}(\text{HCO}_3)_2$, magnesium bicarbonate, as the deacidification agent, MC cellulose for a strengthening agent, with Mesityl NBS and Rewin EL as cationic and anionic fixatives (Wagner *et al.* 2008). The fixatives allow artifacts with aniline dyes and stamps to pass safely through the aqueous treatment. Banik (2005) compares the Neschen process to the Papersave® process, the Bookkeeper® method, and the Libertec® process, finding that Neschen is comparably satisfactory to the Papersave® process.

The Bückerburg treatment is scaled up to mass treatment level by using the Neschen C-900 automated deacidification unit (Lojewski and Gucwa 2003). According to the aforementioned authors, deacidification takes three and a half minutes, during which time the documents travel through a single bath with the three treatment components: the alkaline agent, the two ionic fixatives, and the sizing agent. This is followed by a four minute drying channel of 50°C warm air. By this machine it is possible to deacidify 400 single A4 sheets per hour; it is also possible to treat larger originals, such as newspapers, up to 105 cm wide.

Table 4. Aqueous Applications of Alkaline Agents

Chemical formula	Alkaline agent → Alkaline reserve	Application method	Notes on use	Literature references
CaCO ₃	Calcium carbonate	Aqueous solution	Only slightly soluble (0.00015g/L)	Reissland 1999; Hey 1979
MgCO ₃	Magnesium carbonate	Aqueous solution	Only slightly soluble (0.04g/L as 3MgCO ₃ ·Mg(OH) ₂ ·3H ₂ O, 0.00106g/L as MgCO ₃)	Hey 1979
Ca(OH) ₂	Calcium hydroxide → calcium carbonate	Aqueous solution—saturated solution diluted 1:1 with water (approx 0.01M); also used in the Vienna process	High pH (10-12.34) can adversely affect some colorants; slight yellowing of papers; simple to prepare; good retention of alkalinity upon aging; solubility at room temperature 0.017g/L	Reissland 1999; Lienardy and van Damme; Hey 1979; Anguera 1996
Ba(OH) ₂	Barium hydroxide → barium carbonate	Aqueous solution or 1% in methanol	Toxic, high pH leading to yellowing and color change; solubility at room temperature 0.39 g/L	Lienardy and van Damme 1990; Kelly 1972
Ca(OH) ₂ + Ca(HCO ₃) ₃	Calcium hydroxide (bath 1) + calcium bicarbonate (bath 2) → calcium carbonate	Barrow two bath method (aqueous solutions)	Insufficient reserve due to low solubilities of “lime water” and Ca(HCO ₃) ₃ , limiting the amount of CaCO ₃ that can be deposited; high pH of first bath (> pH 12) can have adverse effects	Lienardy and van Damme 1990; Kelly 1972
CaCl ₂ + (NH ₄) ₂ CO ₃	Calcium chloride + ammonium carbonate → calcium carbonate	Double decomposition (aqueous solutions)	Concerns of residual chlorine	Lienardy and van Damme 1990; Kelly and Fowler 1978
Ca(HCO ₃) ₂	Calcium bicarbonate → calcium carbonate	Aqueous solution	pH not greatly increased (maximum 8.1), low alkaline reserve; 1.086g/L when saturated with CO ₂ ; pH of solution 5.88	Reissland 1999; Lienardy and van Damme 1990
Mg(HCO ₃) ₂	Magnesium bicarbonate → magnesium carbonate	Aqueous solution; also used in the Neschen (Bückebug) and Vienna processes	Initial spike in pH (max. 9.9-10.5), low alkaline reserve after aging, yellowing of paper; “gritting” observed; challenging to prepare; poor light stability of treated paper; 18.3g/L when saturated with CO ₂ (approx. 0.04M); pH of solution 7.07	Reissland 1999; Lienardy and van Damme 1990; Daniel <i>et al.</i> 1990; Hey 1979
Ca(HCO ₃) ₂ + Mg(HCO ₃) ₂	Calcium-magnesium bicarbonate → calcium-magnesium carbonate	5:1 Ca/Mg w/w	Combines lower pH of Ca(HCO ₃) ₂ and more substantial alkaline reserve of Mg(HCO ₃) ₂ ; pH of solution 8.0-8.5	Anguera 1996
Na ₂ B ₄ O ₇	Sodium tetraborate (borax) → NaOH	Aqueous solution	Decrease in DP after humid aging (total & immediate loss of strength in wood pulp paper), change in inks & pigments, yellowing, caution required with coated papers & tempera colors (borax can cause oxidation of protein compounds, e.g. casein); (30g/L); solution pH 7.1	Lienardy and van Damme 1990; Daniel <i>et al.</i> 1990

Non-Aqueous Liquid-Based Systems

At least part of the motivation for considering non-aqueous solvents for the distribution step has been related to perceived drawbacks with aqueous systems. Aqueous treatment systems, being very polar, can suffer from solubility of some inks and some binding materials, changes in paper density or flatness, and the cost, difficulty, and the relatively large time requirement to evaporate the water from the paper. Though some organic solvents interact with some inks and colorants in paper, many of them do not affect hydrogen bonding at all, and in most cases the heat of evaporation is much lower than that of water. Descriptions of widely used solvent-based deacidification systems have been published (Baynes-Cope 1969; Smith 1970; Williams 1971; Cunha 1987; Smith 1988; Albrecht and Turkovics 1991; Brandis 1994; Blucher and Vogelsanger 2001; Banik 2005).

Non-aqueous treatments can be placed into three main classes: *liquid solutions*, *liquid suspensions*, and *gas phase* treatments. In principle, interactions with various inks, colorants, and binders can be minimized by selecting a solvent system that has large differences in its solubility parameters, in comparison to likely components of the document (Barton 1975). Gas phase treatments, which will be discussed in a later section, can be complicated to administer, but in theory should have little interactions with sensitive media.

Suspensions of alkaline agents can be successfully prepared in non-polar solvents such as perfluorinated hydrocarbons, silicone-based solvents, and to some extent by simple hydrocarbons such as heptane. These solvents have limited media interactions, but the use of suspended particles may result in less even distribution of alkaline agents and more surface deposits (Kelly 1978). In the cited author's words, "poor solvents cause the alkali to lag behind the solvent front in penetrating the paper." Largely this is due to the polar nature of many alkalis and the non-polar solvents that are employed for their distribution. By contrast, Kundrot (1985) and Sequeira *et al.* (2006) patented systems based on intentionally distributing particles of alkaline material that were dispersed, rather than dissolved, in an inert solvent.

True alkaline solutions are likely to lead to the most even distribution of chemicals throughout paper, if applied properly. Polar protic solvents that dissolve alkaline species such as ethanol, methanol, and isopropanol are familiar to conservators and have the advantage of causing cellulose to swell, allowing alkaline agents to better penetrate into the fiber structure (Lichtblau and Anders 2006). Polar ink components, however, make the use of such solvents difficult on a mass deacidification scale. Complicated mixtures, which are more likely cost-prohibitive, are often necessary to achieve dissolution of alkaline species in non-polar solvents that won't interact with inks and media.

Each non-aqueous deacidification treatment, summarized in Table 10 at the close of this section, is an attempt to balance alkaline agent solubility/distribution with suitable solvent selection. The following sections discuss many of the distribution methods, in roughly their order of invention or development.

Wei T'o system

The Wei T'o system involves treatment of paper with a liquid alkaline agent, such as methylmagnesium carbonate (MMC), in a solvent (Kelly *et al.* 1977). As noted by Cunha (1987) and Batton (1990), the Wei T'o system has undergone various evolutions. Richard Smith, the inventor of the process, first used magnesium methoxide as the deacidifying agent, but this material was found to be too moisture-sensitive. George Kelly of the Library of Congress was working on a similar process and found that the reagent could be made more stable by reacting it with carbon dioxide. More recently the Wei T'o system has been further modified with the use of methoxymagnesium methylcarbonate (MMMC), which is even more stable against moisture. Initially the solvent was one of several Freons, but later this was changed to hydroxychlorofluoro compounds (Dufour and Havermans 2001). These solvents are generally accompanied by a methanol co-solvent to ensure full dissolution of the alkaline agent (Hon 1989).

The process was initially developed for spray and immersion single-item treatment techniques. In 1982-1983, Princeton University Library's adoption of the system resulted in the development of spray-based mass deacidification equipment (Batton 1990). A further development was the application under pressure, followed by removal of excess reagent by vacuum distillation (Arnoult 1987; Cunha 1987; Batton 1990; Turko 1990; Lienardy 1994; Bukovský 2005). When the pressure-modified version of the Wei T'o process is applied to multiple books, the first step is vacuum drying (Cunha 1987). This step, taking 36-48 hours, reduces the moisture content of the books to 0.5% (Dufour and Havermans 2001). About 30 books at a time are placed in a processing tank, air is removed, the tank is filled with the non-aqueous deacidifying solution, and the system is pressurized to impregnate the pages. Once the treatment is judged to be complete, the system is drained, the solvent is recovered, and the books are dried under vacuum. The impregnation and after-drying steps take about one hour each. The volumes are removed from the treatment chamber and placed spine down in corrugated board boxes to allow moisture content equilibration under ambient conditions for 12-48 hours.

The Wei T'o system has been used successfully in Canada for several years (Smith 1977, 1987; Scott 1987; DeCandido 1988; Morrow 1988); a main concern was that some books needed to be tested for ink solubility (DeCandido 1988; Dufour and Havermans 2001). Wei T'o always requires careful preselection of books and documents due to the presence of methanol as a co-solvent (Hon 1989). Batton (2005) noted that various classes of documents may be excluded from treatment by the Wei T'o system, including items containing brittle paper, coated paper (which were observed to stick together), risky inks, lignin-containing papers (which can darken), and papers from the Near East or India.

Many authors have evaluated aspects of the performance of the Wei T'o system. Their observations are summarized in Table 5 below. It is important to determine which version of Wei T'o was being used before directly comparing these studies, as it has had so many iterations over time.

Table 5. Evaluations of Wei T'o Deacidification

Reference	Observations
Kelly 1972	Sufficient alkaline reserve, retention of pH even after accelerated aging, some ink bleeding, issues of spray system clogging at high RH
Batton 1990	Effective deacidification: sample papers demonstrate a pH range of 9-10 (three pH units above untreated control samples)
Daniel <i>et al.</i> 1990	Under some conditions some treated samples deteriorated more rapidly than untreated samples
Bredereck <i>et al.</i> 1990	Rated Wei T'o as the most effective and reliable among alternatives evaluated
Green and Leese 1991	Good deacidification with MMC and with a related commercially available product.
Lienardy 1991, 1994	Visible deposits and odor were noted during a first set of Wei T'o-treated items evaluated; such problems were not detectable during evaluations of a later set of treated items. Issues of bleeding inks and limited homogeneity in distribution of alkaline reserve
Pauk and van de Watering 1993	Sharp odor associated with Wei T'o treated volumes
Kaminska and Burgess 1994; Lienardy 1994	Wei T'o treatment has good effect on paper stability
Brandis 1994	Some uneven distribution; deficiencies in observable condition of treated books relative to other evaluated deacidification methods
Bukovský 1997	Tendency of the alkaline agent to promote photo-yellowing, related to the ultraviolet component of incident light
Clark <i>et al.</i> 1998	In studying the distribution of related magnesium compound (ethoxy-magnesium ethylcarbonate) on a microscopic scale, the alkaline agent was congealed as non-uniform deposits. Penetration into the paper by the agent only partial
Bukovský 1999a,b, 2001; Rychly <i>et al.</i> 2006	Acceleration of aging in some treated samples attributed to alkaline conditions and the promotion of oxidation

Sablé system

Closely related to the Wei T'o system is the Sablé process. Developed in France by the Centre de Recherché sur la Conservation des Documents Graphiques and CIM-Mallet, it uses a combination of MMMC and methyl ethoxide magnesium carbonate (MEMC). The solvent has been changed from Freon-12 and methanol to Freon-134a and ethanol. Like Wei T'o, the MMMC or MEMC produce $Mg(OH)_2$ by hydrolysis, which then reacts with carbon dioxide to form an alkaline reserve of $MgCO_3$ (Dufour and Havermans 2001).

FMC or Lithco process

In 1990, the US Library of Congress issued a request for proposals for mass deacidification of their holdings of paper-based books. One of the companies that responded to this request was the FMC Corporation, proposing a system in which a magnesium compound (initially magnesium butoxytriglycolate or MG-3, later magnesium butyl glycolate or MBG) was dissolved in a solvent (Anon. 1991; Kamienski and Wedinger 1993; Wedinger 1993; Wedinger *et al.* 1993; Brandis 1994; Kaminska and Burgess 1994; Lienardy 1994; Dufour and Havermans 2001). Related technology from

the Lithco Company was earlier described by Wedinger (1989). The chosen solvent was a perfluorinated compound (Freon), but due to environmental concerns this was later switched to heptane. First MG-3 and then MBG were found to have suitable solubility in these solvents, without requiring a polar co-solvent. The much higher boiling point of the magnesium compound ensured that it remained in the paper once the solvent was evaporated. Books, kept closed during treatment, were pre-dried, treated with the deacidification solution, rinsed with the solvent, and dried a second time to drive off residual solvent. The drying steps were performed using a dielectric heating process, utilizing radio-frequency waves to reduce the moisture content of the books to 2%. Evaluations of the FMC process are summarized in Table 6 below.

Table 6. Evaluations of FMC or Lithco Deacidification

Reference	Observations
Wedinger 1993; Kaminska and Burgess 1994	Successful deacidification
Wedinger 1993	Heptane-based system able to achieve a suitably high alkaline reserve, while avoiding odor problems associated with earlier systems
Brandis 1994	Treatment not always uniform, some damage to the condition of the books observed
Lienardy 1994	Residual odor, no residual powder deposits, only 1 of 30 documents had affected ink. Treatment judged to be good, but not as successful overall as DEZ or Bookkeeper.
Tse <i>et al.</i> 1994	Process causes serious damage to wax seals, pencil crayons, color laser copies, new parchment, and polystyrene materials.
Dufour and Havermans 2001	Some acceleration of degradation and photo-yellowing, attributed to excessively high pH.

The FMC process was intended to not only deacidify but also to strengthen the paper fibers (Wedinger 1991). The company's documents state that the similarity of the MG-3 structure (a polymeric repeating group with two oxygen's separated by two carbons) to that of cellulose allows it to interact with cellulose through hydrogen bonding. There does not seem to be any substantiation of this statement in the literature.

Battelle or Papersave® process

The Papersave® process, developed by Battelle Ingenieurtechnik GmbH in Frankfurt, Germany is simply referred to as the Battelle process in the older literature. This system uses magnesium ethoxide as its primary component, in a complex with titanium alkoxides (both ethoxide and isopropoxide), which act as surfactants to dissolve the magnesium ethoxide in hexamethyldisiloxane (HMDO). Being fully soluble in HMDO, there is no need to add any alcohols as co-solvents into the system, which reduces the likelihood of media bleeding (Schwerdt 1989; Wittekind 1994; Wittekind *et al.* 1994; Liers and Schwerdt 1995; Havermans *et al.* 1996; Theune *et al.* 1996; Dufour and Havermans 2001; Lichtblau and Anders 2006). The full complex formulation is referred to as magnesium ethoxide titanium ethoxide (METE), in which the ratio of magnesium to titanium is approximately 1:1. Lichtblau and Anders (2006) show this complex in a clear graphic form. This METE complex reacts with ambient humidity to form $Mg(OH)_2$, which then is converted by atmospheric carbon dioxide to an alkaline

reserve of MgCO_3 . The system is available in Switzerland through Nitrochemie Wimmis under the name of Papersave® Swiss and in Leipzig, Germany through Zentrum für Bucherhaltung (ZfB). ZfB was founded in 1997, while the Nitrochemie deacidification plant opened in 2000 after acquiring a license from ZfB (Lichtblau and Anders 2006).

To begin the process, the books are pre-dried for two days in vacuum, during which they are gradually warmed to 60°C (Havermans *et al.* 1996; Lichtblau and Anders 2006). The normal equilibrium moisture content of the books is thereby lowered from the general 5-7 % (w/w) to less than 0.5%. For the impregnation step, the chamber is flooded with the treatment solution of METE in HMDO. After a few minutes the liquid is drained away, and the system is dried under vacuum. The treated books are allowed to equilibrate with ventilated air for three weeks before the process is considered to be complete. New improvements involve humidity control during this reconditioning step, as it is during reaction with atmospheric water vapor that the actual neutralization and alkalization takes place (Lichtblau and Anders 2006). Additionally, as alcohol is formed during the hydrolysis of METE, ventilation is required in this final step to allow for full evaporation.

Liers and Schwedt (1995) describe the processing equipment as being “a substantially improved version” of that used in the Wei T’o process. Porck (1996) notes that the Battelle system differs from the Wei T’o system in having better recycling, microwave drying, and process control. The microwave heating was abandoned, however, due to overheating of staples and other metal fasteners. Various studies examining the effectiveness of the Battelle or Papersave® process are outlined in Table 7 below.

Table 7. Evaluations of Battelle or Papersave® Deacidification

Reference	Observations
Theune <i>et al.</i> 1996	Uniform distribution of the alkaline product in treated paper, improved mechanical properties (with the exception of folding endurance) relative to the control after accelerated aging
Havermans <i>et al.</i> 1996	Final pH of about 9.3, remaining stable even after artificial aging. Residual odor observed in 42 of 49 tested books, discoloration noted on 8 books, bleeding on 4 books, white deposits on 1 book. Newton rings on 2 out of 10 art paper books treated. Books with rough paper noted to benefit greatly, while smooth paper books showed less benefits with accelerated aging. In many cases magnesium concentration was twice as high at the edges of books relative to the middle parts. Many treated books were found to have weakened, even before accelerated aging
Liers and Vogelsanger 1997	Treated books degrade about four times more slowly than untreated controls subjected to accelerated aging; the degree of polymerization of the cellulose was unaffected by the treatment
Foster <i>et al.</i> 1997	Treatment tends to produce a moisture-resistant coating on items
Banik 2005	Differing results in the Papersave® process, depending on the company applying mass treatment: Papersave® Battelle was satisfactory, whereas Papersave® ZfB provided insufficient deacidification
Lichtblau and Anders 2006	Final pH of papers is between 7-9, but some papers exceed pH 9 for a short period after treatment (while the transformation of $\text{Mg}(\text{OH})_2$ to MgCO_3 is completed); alkaline reserve of 0.5-2% (w/w)

Bookkeeper®

The Bookkeeper® process (Cunha 1987, 1987; Turko 1990; Lienardy 1994; Anon. 1994) involves the use of a magnesium compound in n-propanol (Polovka *et al.* 2006) or perfluoroheptane (Dufour and Havermans 2001). Unlike the other processes described above, while the Bookkeeper® process *does* use a non-aqueous liquid, the alkaline agent is not dissolved. Instead, the process employs a fine suspension of alkaline particles. The alkaline agent consists of insoluble MgO particles, which are understood to form Mg(OH)₂ by *insitu* reaction with moisture from the paper. Decandido (1988) notes that the process does not require pre-drying, and no toxic or explosive chemicals are involved. The Bookkeeper® solution is available for in-house treatment by spraying and is also available for mass treatment. To implement the Bookkeeper® mass process, the books are inspected and secured to a framework that when complete resembles a Christmas tree; larger books, as well as archival documents, are treated in a horizontal chamber. The assembled books are placed in the chamber, the system is evacuated, and a suspension of very fine MgO particles is added in a suitable liquid, which initially was Freon. The system is then agitated gently for five to twenty minutes to distribute the suspension throughout the volumes. A bobbing motion of the books in the recirculating liquid helps to distribute the suspension among the pages. Then the system is drained and evacuated for 90 minutes to remove the suspending medium.

As noted by Whitmore in his contribution to an evaluation report for the Library of Congress (Buchanan *et al.* 1994) the Bookkeeper® process faces two intrinsic challenges: transporting the particles by means of fluid flow, and getting the transported particles to stick to the paper. Neither of these processes is well understood. While it is known that the amount of alkaline agent transferred can differ, depending on the characteristics of a book, the operator does not have a good way to control the outcome. In addition, the relatively large size of the deposited MgO particles, compared to other technologies that apply alkaline agents in solution form, has raised questions about mechanisms and rates of equilibration within paper under relatively dry conditions of storage. The latter concerns can be at least partly satisfied by noting the effectiveness of placing sheets of CaCO₃-containing paper between the pages of a document to be protected (Page *et al.* 1995; Anon 1995b; Middleton *et al.* (1996). The fact that such inter-leaving can affect the Brønsted acidity of paper several sheets away makes it easier to accept that distribution of micrometer-sized particles throughout the document will essentially treat the whole of the material and not leave untreated “gaps” between the deposited particles.

In 1995, improvements were made to the fluid dynamics of the treatment process, meaning the concentration of magnesium oxide in the suspension could be decreased by 50%, while maintaining a sufficient alkaline reserve (Porck 1996). This development reduced the problem of white deposits on the treated paper and book covers; these issues had been noted particularly on coated papers (Pauk 1996). Further improvements included a reduction in the MgO particle size. Evaluations of the Bookkeeper® process are found in Table 8, below.

Table 8. Evaluations of Bookkeeper® Deacidification

Reference	Observations
Buchanan <i>et al.</i> 1994	Distribution of the alkaline particles somewhat non-uniform, with a lower amount of the MgO present in the critical spine areas of treated books
Cunha 1989	Uniform coverage of alkaline particles in treated books; pH range of 9-10; initial hydrophobicity of sized papers not disturbed; Treated books performed better in folding endurance tests than controls after accelerated aging.
Hon <i>et al.</i> 1989; Harris and Shahani 1994a,b	Performance of Bookkeeper® system evaluated
Pauk and van de Watering 1993	Avoids sharp odor associated with Wei T'o system
Lienardy 1994	Ink migrations and residual odor noted in first set of books treated with Bookkeeper; issues not evident in a second set of treated books; even alkaline agent distribution.
Pauk 1996	Reduction of aging-related deterioration with treatment; white deposit
Foster <i>et al.</i> 1997	Treatment of the back sides of painting canvases with related systems tended to produce a moisture barrier, which was not intended
Zumbuhl and Wuelfert 2001	Surfactants used with the system have a major influence on the distribution of the alkaline agent
Dupont <i>et al.</i> 2001	Tested the uniformity of the treatment
Wagner <i>et al.</i> 2008	Non-uniform distribution of the alkaline agent on a microscopic scale

CSC Booksaver®

The CSC-Booksaver® Process is a relatively new non-aqueous deacidification method on the European market. Development of this technique began in the 1990s by the Universitat Politècnica de Catalunya (UPC) together with the Spanish company Conservación de Sustratos Celulósicos (CSC), and has been employed at the Preservation Academy GmbH Leipzig since 2003 (Henniges *et al.* 2004). The Booksaver® process involves the introduction of a solution of propoxy magnesium carbonate in 1-propanol (70% w/w) with a heptafluoropropane propellant (HFC 227). HFC 227 is non-toxic, non-flammable, odorless, and has no ozone depletion potential. The treatment, like that of Bookkeeper®, is offered as both a mass deacidification and as a spray for manual application. In mass treatment, the advantages of this process are the relative stability of the deacidification agent when brought into contact with paper of typical moisture content. This allows the treatment of archives and library materials without an additional pre-drying step required by many of the other mass treatments. Only particularly sensitive artifacts have to be preconditioned, requiring only a mild treatment for about 12 to 24 hours and at a maximum of 50°C. Dupont *et al.* (2002) demonstrate that the spray form of this technique can efficiently deacidify papers without leaving surface deposits, while depositing enough alkaline reserve to protect them from atmospheric NO₂ attack. Henniges *et al.* (2004) also note that this system has potential for treatment of papers suffering from copper pigment corrosion, slowing this detrimental process.

Supercritical carbon dioxide as a deacidification solvent

Selli *et al.* (2000) reported results from innovative deacidification systems employing supercritical carbon dioxide. It is well known that CO₂ and other gases acquire superior solvent properties when they are very strongly compressed (and sometimes heated) into a range where they have properties that are intermediate between that of a liquid and that of a gas. It was found that the supercritical CO₂ was effective in distributing calcium carbonate particles in acidic papers, thus raising the pH and creating an alkaline reserve. Ethanol could be used as a co-solvent.

Impregnation with strengthening agents in non-aqueous systems

Certain strategies for the strengthening of paper are compatible with non-aqueous solvent-based deacidification systems. Clements (1987) showed that brittle paper could be strengthened by impregnating it with a mixture of ethyl acrylate and methyl methacrylate monomers, which then could be polymerized for *insitu* strengthening by means of gamma irradiation. The polymers then functioned as *insitu* strengthening agents in the paper. Smith (1987) states that the Wei T'o system is compatible with the impregnation of methacrylic or acrylic resins into closed volumes, together with suitable fungicides. Ipert *et al.* (2005) showed that certain aminoalkylalkoxy silanes can function as strengthening agents, in addition to their role as sources of alkalinity. Please see the the "Associated or Alternative Treatments" section later for a more detailed discussion on strengthening.

Gas-Phase Treatments

All of the solvent-based systems just described require evaporation, which is energy-intensive. Gas-based systems avoid the need for an evaporation step. As noted by Banik (2005), however, gas-based systems are unlike aqueous immersion techniques insofar as they do not remove acetic acid from the paper, though they may neutralize it. Acetic acid, again, may stem either from oxidative degradation of polysaccharides, or may be adsorbed onto the paper from the environment.

Diethyl zinc (DEZ) or Akzo process

The DEZ or diethyl zinc process was developed first by the Library of Congress and then by Akzo Chemicals Inc. in the mid-1970s. It is based on the distribution of diethyl zinc (DEZ) in the gas phase (Smith 1987; Sparks 1987; Anon. 1999a; Hon *et al.* 1989; Turko 1990; McCrady 1992; Yamazaki *et al.* 1992; Harris and Shahani 1994a,b; Kaminska and Burgess 1994; Lienardy 1994; Stroud 1994; Havermans *et al.* 1995; Dufour and Havermans 2001). The first step in the process, the drying phase, involves placing the books to be treated in a sealed container, where the air is first replaced by nitrogen, and then a vacuum is applied at 40°C for a sufficiently long time to reduce the moisture content of the paper to approximately 0.5%(w/w) (Cunha 1987). This drying can take between 12 and 32 hours (Brandis 1994; Dufour 2001). Due to the reaction of DEZ with water, the amount of residual water determines how much of the alkaline agent becomes incorporated into the paper. At these low preconditioned moisture contents most of the DEZ is expected to form a ZnO alkaline buffer, which later on in the process can react with excess water to form zinc hydroxide:



In the second stage of the process, the permeation step, the dried volumes are treated under vacuum at -20 to -30°C with neat DEZ vapor, which is added gradually, with the progressive evolution of ethane. This stage may take up to 16 hours (Brandis 1994) and yields an alkaline reserve of up to 3.5% ZnO (Dufour 2001). Experimental results suggest that incorporation of about 1% ZnO is sufficient to obtain a substantial benefit of the treatment, and that a level of 2% is enough to reach a plateau level of relatively high stabilization against accelerated aging (Anon. 1999b). Any DEZ that is removed along with the ethane is separated and recycled. Once the reaction is judged to be complete, the remaining DEZ is purged by warm dry nitrogen gas, followed by vacuum application. The third stage consists of an initial six-hour introduction of water vapor and carbon dioxide into the chamber, followed by a three-day humidification in ambient air to restore a typical level of moisture (Havermans *et al.* 1995).

Due to the amphoteric nature of ZnO, it not only can react with acids to form salts, but also with alkalis to form zincates:



The pH of the paper is therefore buffered between 7.5 and 9.5, protecting the paper from both proton-catalyzed hydrolysis and alkaline-induced degradation reactions. Various studies evaluating the efficacy of DEZ deacidification are summarized in Table 9, below.

Table 9. Evaluations of DEZ Deacidification

Reference	Observations
Smith 1987	Advantage of gaseous process is uniform and pervasive treatment
Cunha 1987	Extends useful lifetime of acidic document by a factor of about 3 to 5
Yamazaki <i>et al.</i> 1992	Treatment protected some, but not all, samples against effects of accelerated aging
Lienardy 1994	Judged one of two successful deacidification systems, among seven systems evaluated. Concern that ZnO may impart light sensitivity to treated items; iridescent marks on very glossy papers.
Harris and Shahani 1994a	Process improvements overcome issues with iridescent marks on very glossy papers, leaving DEZ one of the only processes known to be effective for treating coated papers.
Brandis 1994	Acceptable rank for pH levels, improvement in paper life, and post-treatment moisture content. Fair levels of alkaline reserve. Poor grades on odor post-treatment, extreme levels of temperature (100°C maximum temperature recorded in a book), bleeding of media, and overall condition of whole books.
MacInnes and Barron 1992	Advanced methods to demonstrate quite uniform distribution of alkaline agents in treated documents
Havermans <i>et al.</i> 1995	Reproducible, successful neutralization of acids and homogeneous distribution of ZnO particles through paper fibers. DEZ as de-facto standard for successful deacidification. Treatment remains effective after exposure to high levels of air pollutants.

The DEZ system is potentially hazardous, since DEZ reacts violently with water and ignites on contact with air in a violent exothermic reaction (Havermans *et al.* 1995). There was a series of accidents in 1985 and 1986 at a DEZ pilot plant at NASA's

Goddard Space Flight Center; suggested causes included procedural errors, equipment malfunction, and poor design of the delivery and recovery system for DEZ (Cunha 1987). Thomson (1988) noted that hazards can arise due to excessive residual moisture in the books to be treated and ZnO deposits forming on the processing equipment. The same author observed poorer results for folding endurance, brightness, and pH relative to the same test of documents treated by the Wei T'o system. Perhaps for these reasons, the system was withdrawn from the market (Stroud 1994) with the closure of the Akzo plant in Texas in 1993 (Dufour 2001).

Dry Ammonia Ethylene Oxide (DAE) and Book Preservation Associates (BPA) methods

The National Diet Library in Japan adopted a treatment system with dry ammonia and ethylene oxide (Okayama *et al.* 1994, 1996a,b; Anon. 1999b; Anon. 2001). Commercial operation at Nippon Filing Co. Ltd. began in 1998, at a rate of approximately 400,000 volumes per year. Called the DAE process, the two reagents are introduced in a vacuum chamber over a 48 hour period to form stable ethanolamines *insitu*. It was shown that mono-, di-, and triethanolamine were generated in the treated paper (Okayama *et al.* 1994, 1996a). The ethanolamines formed by this Japanese process are described as more stable than those produced by the earlier Book Preservation Associates (BPA) method, despite the fact that the reagents used in each technique are the same (Anon. 1999b). Based on accelerated aging tests, the rate of deterioration was predicted to be decreased by a factor of five or more. Also, the extract pH of the paper was increased. After treatment, papers were found to have a pH of 8.0-8.7, which they maintained with only a gradual decrease during accelerated aging (Yasue 1998). Benefits of pest and mold control, along with the practical need for little pre-selection, have been noted (Anon. 1999b). Ipert *et al.* (2005) note that while this process results in increased interfiber bonding, the dangers involved in mixing these two gases are not to be underestimated. An initial decrease in brightness has been observed in treated papers as well as a dimensional increase of 2% (Anon. 1999b).

Alkaline gases

Kusterer and coworkers patented systems in which books and other documents are exposed to gaseous hexamethylenetriamine (Kusterer and Hind 1972), or morpholine (Kusterer and Sproull 1973; Walker 1977). Though such systems appear to effectively neutralize Brønsted-acidic species present in the paper, once the relatively volatile alkaline agents are evaporated from the paper there does not seem to be any residual alkaline reserve left behind in the documents.

Graft polymerization in the gas phase

In contrast to the systems discussed so far, gaseous graft polymerization systems for deacidification involve a direct reaction with the cellulose or hemicellulose in the paper (Carter 1996a; Porck 1996; Cheradame *et al.* 2003; Rousset *et al.* 2004; Ipert *et al.* 2005). The essential concept behind graft co-polymerization is that cellulosic fibers can be strengthened by grafting other polymeric chains to the cellulose. These polymeric chains are introduced into the paper initially as monomers. For instance, the British library has experimented with monomeric ethyl acrylate and methyl methacrylate. First

the moisture content of the books is reduced, followed by gaseous introduction of the acrylic monomers. Overnight, the monomers diffuse through the paper fibers, after which the papers are irradiated with low intensity gamma rays (*e.g.* from a cobalt-60 source) to induce free-radical polymerization. The resulting long-chain polymers interweave with the cellulose chains, giving a strengthened paper structure. Residual monomers are removed by ventilation and evaporation. Disadvantages of the process are the minor depolymerization of cellulose caused by gamma irradiation, as well as a 10-20% increase in paper weight.

Other gaseous reagents have the capability of both increasing strength and introducing an alkaline reserve. Amino alkyl alkoxy silanes, generally in ethanolic solution, can be used for such purposes. Rousset *et al.* (2004) demonstrated that 3-amino propyl trimethoxy silane (ATMS) was capable of providing sufficient alkaline reserve, while also acting as a polymeric strengthener. A potential advantage of such systems is that the alkaline agent becomes permanently covalently bound to the paper at a molecular level. These treatments aim not only to retard degradation processes, but also to increase the mechanical strength of the treated papers. Ipert *et al.* (2005) showed that treatment with ATMS resulted in significant increase of tensile strength, an effect that lasted even after accelerated aging. The aforementioned authors were not ready to fully attribute this effect to covalent bonding with the fiber network; an entanglement effect may provide the same results.

Forced air (Bell) or Libertec®

Perhaps the simplest gas-based system is the use of air to blow a deacidifying agent against the paper surfaces (Kundrot 1985; Bell 1996; Banik 2005). These systems use dry application of sub-micron particles of magnesium oxide and magnesium carbonate. Bell (1996) claimed that such a system, when applied to an open book, can result in a thorough distribution of the alkaline agent, including within the spine area of the book. These systems are employed by several European companies, including Libertec Bibliotheksdienst and SOBU, of Nürnberg, Germany, but have been shown to be considerably less effective at achieving desired levels of deacidification than aqueous and non-aqueous processes (Banik 2005). This is partially due to the fact that acetic acid in the paper is not eliminated during dry application of alkaline agents. Ramin *et al.* (2009) tested treatment quality of five processes (Libertec®, Papersave® Swiss, Bookkeeper®, CSC Booksaver®) and found that Libertec® passed the quality standards of achieving a pH of greater than 7 and an alkaline reserve of at least 0.25% MgCO₃, but notes that the dispersion processes tend to deposit the alkaline agents on the paper surfaces, as opposed to the solvent procedures that actually penetrate the fiber networks.

Interleaving with Alkaline Sheets

Remarkably, one of the quickest and safest ways to overcome the effects of Brønsted acidity in an individual book that happens to be highly acidic is to place suitably thin sheets of alkaline paper (containing calcium carbonate) between the pages (Page *et al.* 1995; Anon 1995b). In demonstrating the effectiveness of such an approach, Middleton *et al.* (1996) provided evidence that an alkaline solid material can influence the pH of paper up to several page thicknesses in distance. In other words, it appears

highly likely that some equilibration occurs due to the presence of moisture in the air under ambient conditions. Indeed, the approach was shown to become increasingly effective as the humidity was increased.

A related approach developed by Langwell involved insertion of sheets that had been saturated with cyclohexylamine carbonate between the pages of a book to be deacidified (Langwell 1973; Cunha 1989). Unfortunately, this vapor phase deacidification process was found to be carcinogenic. Hansen (2005) combined calcium carbonate and sodium bromide in an effort to provide both deacidification and antioxidation for iron gall ink containing papers. Employing both temporary and long-term interleaving, Hansen showed that there is a clear migration of ions at high relative humidities, as the stabilization effects were demonstrated even after the interleaving papers had been removed. Greater stabilization was achieved the longer the interleaving papers were left in place.

Alkaline paper has also been successfully impregnated with zeolite molecular sieves. The microchambers in these finely porous particles are able to trap and neutralize acidic pollutant gases that cannot be neutralized by alkalinity alone. Zeolites are microporous crystalline aluminosilicate structures and provide selective molecular trapping based on size and polar properties (Dyer 1988). Other molecular traps include activated carbon and synthetic, acid-resistant zeolites, which are cast into the paper matrix containing alkaline buffers (Passaglia 1987; Guttman and Jewet 1993). Molecular traps have been used for preventing and slowing down degradation and have been successfully used for paper materials, books, and photographs.

Table 10. Non-Aqueous Applications of Alkaline Agents

Chemical formula or abbreviation	Alkaline agent → alkaline reserve	Application method (Trade Name)	Potential issues	Literature references
MMMC; EMEC; MMC	Methyl magnesium methyl carbonate, ethoxy magnesium ethyl carbonate, magnesium methyl carbonate; magnesium ethyl carbonate → magnesium carbonate	Non-aqueous solution (Wei T'o No 2; No 3/4; No 10; No 11/12)	High pH (7.4-10.4), potential media bleeding, changes in colors sometimes observed, requires careful preselection due to alcoholic co-solvents, some surface deposits; good mechanical strength, good alkaline reserve	Reissland 1999; Lienardy and van Damme 1990; Dufour and Havermans 2001; Brandis 1994
MMMC + MEMC	Methyl magnesium methyl carbonate + methyl ethoxide magnesium carbonate → magnesium carbonate	Non-aqueous solution (Sablé)	Requires careful preselection due to alcoholic co-solvents	Dufour and Havermans 2001
MG-3 or MBG	Magnesium butoxytriglycolate or magnesium butyl glycolate	Non-aqueous solution (FMC or Lithco process)	Photo-yellowing due to high pH; residual odor noted; even distribution not always achieved	Dufour, Havermans 2001; Lienardy 1994; Brandis 1994; Anon. 1991
MgO	Magnesium oxide → magnesium hydroxide and magnesium carbonate	Non-aqueous suspension (Preservation Technologies, Bookkeeper®)	Modified for smaller particles to avoid surface deposition; acetic acid detected (GC-MS) following accelerated aging of treated samples	Anon. 1994; Dufour and Havermans 2001; Banik 2005; Buchanan <i>et al.</i> 1994

Chemical formula or abbreviation	Alkaline agent → alkaline reserve	Application method (Trade Name)	Potential issues	Literature references
Ba(OH) ₂	Barium hydroxide → barium carbonate	Solution in methanol	Toxicity of barium salts, media solubility in methanol, pH as high as 13; adequate alkaline reserve;	Baynes-Cope, 1969; Kelly 1972
CaCO ₃ + MgO	Calcium carbonate and magnesium oxide	Dry application in air stream (Libertec®)	Acetic acid detected (GC-MS) following accelerated aging of treated samples	Banik 2005
CaCO ₃	Calcium carbonate	Solution in super critical carbon dioxide	May require ethanol co-solvent—problematic for some inks and dyes	Selli <i>et al.</i> (2000)
NH ₃ (g)	Ammonia	Gaseous	Too volatile—alkalization doesn't last	Lienardy, van Damme 1990; Smith 1988; Kelly 1972
DEZ	Diethyl zinc → zinc oxide (ZnO) and zinc carbonate (ZnCO ₃)	Gaseous	Explosive if used incorrectly, mass treatment only, not modified for bench use; amphoteric nature of ZnO buffers in pH range 7.5-9.5	Lienardy and van Damme 1990; Dufour, Havermans 2001
O(CH ₂ CH ₂) ₂ NH (a heterocycle)	Morpholine	Gaseous	Insufficient reserve (evaporates), particularly poor performance with mechanical wood pulp, health hazard	Lienardy and van Damme 1990
METE in HMDO	Magnesium titanium ethoxide in hexamethyl disiloxane → magnesium carbonate and titanium dioxide (inert filler)	Non-aqueous solution (Battelle, Papersave®)	pH 7.5-9	Dufour and Havermans 2001; Wittekind 1994
NH ₃ + C ₂ H ₄ O	Ammonia + ethylene oxide → ethanolamines	Gaseous (DAE or BPA processes)	Initial increase in brightness, dangerous reaction, 2% dimensional increase; pH 8.0-8.7 on aging	Okayama <i>et al.</i> 1994; Anon. 1999b
C ₆ H ₅ NH ₄ CO ₃	Cyclohexylamine carbonate	Gaseous	Lower volatility than ammonia, but still too volatile: alkalization doesn't last; hydrolyzes with atmospheric moisture to produce a carcinogen	Lienardy and van Damme 1990; Smith 1988; Kelly 1972
	Propoxy magnesium carbonate	Non-aqueous solution (CSC Booksaver®)	Efficient deacidification; no surface deposits; enough alkaline reserve to protect from atmospheric NO ₂ attack; pH 8.78-10.5	Dupont <i>et al.</i> (2002)
ATMS	3-aminopropyl trimethoxy silane and other aminosilanes	Non-aqueous liquid or gaseous	Various treatments in development; advantage of not containing magnesium; ATMS binds covalently to or entangles with cellulose to provide increased tensile strength properties	Cheradame <i>et al.</i> (2003); Rousset <i>et al.</i> (2004); Ipert <i>et al.</i> (2005); Yoon <i>et al.</i> (2008)
	Calcium and magnesium alkoxides, with quaternary ammonium bromide antioxidants	Non-polar suspension or polar solution options (Inksave®)	In development for iron gall ink treatments; solution for more even distribution, suspension for when polar solvents cause media solubility	Lichtblau and Anders 2006; Reissland <i>et al.</i> 2006; Kolar <i>et al.</i> 2006

JUDGING THE SUCCESS OF A DEACIDIFICATION PROGRAM

Criteria for Success and Evaluation Methodologies

Success of any deacidification program requires a careful definition as discussed in many earlier articles (Cloonan 1990; Schwerdt 1989; Turko 1990; McGee 1991; Botti *et al.* 2006; Cedzova *et al.* 2006). Various institutions have developed standards, particularly where mass deacidification processes are concerned (Anon. 2004; Andres *et al.* 2008). Criteria of two types can be considered. On the one hand, tests and observations are needed to verify that a deacidification procedure has been properly and adequately implemented, *i.e.* quality control. On the other hand, at least at some point, there needs to be a demonstration that the treatment has the desired effect of prolonging the useful life of paper-based material, while not adversely affecting other elements or components of a book, including the binding structure, adhesives, book cloth, *etc.*

The largest numbers of beneficiaries of deacidification are materials to be found in libraries and archives. Therefore, in addition to technical performance, criteria for success must include affordability, sustainability, ease of selection process, and mechanization to ensure that production levels can meet collection needs (Cloonan 1990). More importantly, preservation librarians, archivists, and conservators must recognize that even amidst the success of individual and mass deacidification, deacidification is selectively appropriate and only one treatment possibility among many other available approaches (Strauss 2000).

While assessing the success of deacidification as a treatment option is critical, preservation administrators and conservators must also assess the efficacy of deacidification as a conservation strategy as opposed to reformatting technology to save the intellectual content. Markovian modeling, a stochastic process taking into account time variance and randomness of degradation, has been used in assisting assessment of changes taking place within objects both on a molecular and a macromolecular level (Konsa 2008). Since deterioration processes are complex and take place on all organizational levels of objects, some suggest that an institutional risk assessment based on the Markovian process may offer a strategic modeling for selecting materials for deacidification and a tool to be used to determine the relative success of deacidification in context of other modes of deterioration occurring simultaneously.

Dangers: First, Do No Harm

An overriding aim of conservators, librarians, and curators is that deacidification programs or other actions taken to preserve or restore valuable articles should not damage the items that one intends to protect. In at least one case it was decided not to proceed with a deacidification program, pending resolution of such concerns (Jones 1999). Several studies conclude that deacidification should be avoided for papers that do not need it (Botti *et al.* 2006). Sparks (1990) implored implementers to be informed about the many flavors of mass deacidification technologies and to conduct preliminary tests. At a minimum, he encouraged testing the candidate systems for compatibility with substances found in books, including cellulose, lignin, gelatin, starch, polyvinyl acetate, polyvinyl alcohol, polypropylene, and fluorescent whitening agents. The treatment also should not adversely affect paper's color, brightness, strength, odor, or lack of toxicity. Reissland *et*

al. (2006) include a concise list of potential adverse effects of treatment and the potential causes for each, including color changes, due to the dissolution of colored products as well as pH-induced color changes or the addition of colored substances in treatment, morphological changes, surface deposits, changes in odor, and changes in paper composition. More significantly for art on paper, both color and surface texture can be negatively affected by increasing alkalinity, even if the paper would benefit from deacidification. Some pigments, dyes, and inks can fade or change color with increased alkalinity (Clapp 1977). Surface deposit from spray deacidification and some aqueous treatments may alter the surface appearance of pastels and charcoals. In these cases, a conservator needs to have the knowledge and the skill to determine which deacidification treatment is best and what sort of masking or barrier is needed to limit alkaline penetration to the compromised area. Considering the very wide variety of paper, inks, and binding materials, it is important to eliminate, or at least minimize the need for pre-selection and/or preparation of materials for the chosen deacidification method.

The areas of concern listed above help to explain why, even though they were among the first to be investigated (Schierholtz 1936), aqueous treatment systems have not been more widely considered for mass deacidification of bound volumes or for art on paper. The advent of cyclododecane as a barrier for sensitive pigments, inks, and wax seals (Brückle *et al.* 1999), however, has now enabled a wider range of maps and art on paper to be successfully deacidified using aqueous treatment. Due to the potential adverse affects described above, an aqueous treatment is item-specific; therefore it could not provide the mass delivery system needed to address the estimated 33% of library collections on acidic paper (Walker *et al.* 1985; Smith 1999). A non-aqueous means of deacidification that would not be harmful to pigments and other media was the strongest motivation for the development of silicone-based solvents, as well as the earlier use of perfluorinated hydrocarbons for deacidification programs (Committee for Paper Problems 1968).

Effective Neutralization of Brønsted Acids

As noted earlier, the most widely used procedure for evaluation of paper pH involves the placement of a drop of water or aqueous solution on to the paper surface for a defined period, followed by the use of a flat combination pH-reference electrode (Ramarao and Kumar 1986; Kelly 1989; Sparks 1990; Pauk and van de Watering 1993; Kaminska and Burgess 1994; Okayama *et al.* 1994, 1996a,b; Zappalà 1994; Guerra *et al.* 1995; Anguera 1996; Kozielec 2004; Sundholm and Rahvanainen 2004; Ipert *et al.* 2005; Zappalà and De Stefani 2005). Cunha (1987) and Cedzova *et al.* (2006) recommended end pH values between about 7 and 8, or various wider ranges.

Sufficient Alkaline Reserve

It is well recognized that over time paper can be subjected to continued sources of Brønsted acidity. To render the paper resistant to such acidity and maintain the pH within a suitable alkaline range, it is common to specify a minimum level of “alkaline reserve” in the paper (Kelly 1972, 1989; Sparks 1990; MacInnes and Barron 1992; Vallas 1993; Kaminska and Burgess 1994; Stroud 1994; Havermans *et al.* 1995; Dupont *et al.* 2002; Bukovský 2005; Ipert *et al.* 2005). The quantification of these reserve alkaline species is

difficult to do by simple titration, due to the insolubility of many of them; thus the initial addition of protons from a strong acid, followed by back-titration with a strong base is usually necessary (Liers 1999). Cedzova *et al.* (2006) specified that an equivalent of 2% (w/w presumably) of an alkaline earth carbonate should be present in the deacidified paper. Cunha (1987) recommended an equivalent of 3% or more CaCO₃.

Uniform Distribution

In addition to sufficient quantity of alkaline reserve, it is reasonable to assume that a deacidification agent needs to be well distributed throughout the material to be protected. Otherwise, one might anticipate cracking or other failure in untreated areas. In some cases non-uniform treatment has been observed to result in such visible signs as white deposits (Kelly and Fowler 1978; Porck 1996). Advanced techniques, such as the laser ablation method of inductively coupled plasma mass spectroscopy, have been used to evaluate the uniformity of distribution of magnesium in paper resulting from a deacidification program (Wagner *et al.* 2008).

Cost of Treatment

When it comes time to implement deacidification procedures, cost often becomes an overriding issue (see Smith 1970, 1977; Schwerdt 1989; Bredereck *et al.* 1990; McCrady 1990; Vallas 1993; Okayama *et al.* 1996a; Anon. 1999a). Regardless of the method of delivery, deacidification must be a value-added activity proportionate to the value of the individual item or to the whole of a collection. If it is prohibitively expensive, then libraries and archives will not be able to sustain this treatment option, potentially leading to different technological solutions as libraries attempt to balance the realities of collection maintenance with acquisitions. During the early 1990s the cost of mass deacidification was between \$6.00 and \$10.00 per book. This is a reasonable price when one considers the alternative costs of preservation photocopying (\$65.00), microfilming (\$250.00), or doing nothing (Harvard 1991). Today, the cost for mass deacidification of an average book is approximately \$17, and for archival collections the cost is estimated by the pound at about \$14 (BookKeepers). When compared to the cost of alternative strategies such as digital reformatting at \$ 45.00 per book or doing nothing, it is a low-cost option with great value added.

Safety

Safety is another top priority. In the case of deacidification processes one must take into consideration the safety not only of end-users, but also of the people carrying out the deacidification. For instance, concerns over toxicity and fire hazard of the diethyl zinc process caused some potential users to select alternative processes (Smith 1987; Sparks 1987; Schwerdt 1989). The presence of toxic gases can be of particular concern in the confined spaces of book stacks.

Proving Effectiveness: Accelerated Aging

Accelerating aging tests promise to make it possible to judge the effectiveness of different deacidification programs without having to wait many years for natural aging to take place. When the goal is to compare paper samples having different concentrations of

Brønsted acids or different conditions of deacidification, the two most critical variables are temperature and humidity. Thus, conservation scientists have developed various accelerated aging protocols based on elevated temperatures, in combination with a well defined humidity; the strength and other attributes of the paper are evaluated after being exposed for defined lengths of time (Rasch 1931; Richter 1931; Rasch and Scribner 1933; Shahani *et al.* 1989; Sparks 1990; Zou *et al.* 1994, 2006; Vandeventer *et al.* 1995; Zou *et al.* 1996a,b; Kato and Cameron 1999; Wu *et al.* 1999; Proneiwicz *et al.* 2002; Ipert *et al.* 2005; Zervos and Moropoulou 2006; Ahori *et al.* 2006; Manso *et al.* 2006; Zou *et al.* 1996a,b). Wilson and Parks (1980), among many others, have used accelerated aging tests under controlled conditions of humidity in an effort to estimate which paper samples will degrade faster than others during natural aging.

Zervos (2010) presents a detailed review of accelerated aging, including consideration of what conditions of temperature and humidity should be used, depending on the goals of an investigation. Temperatures of 80°C and 90°C have been used most frequently when carrying out the tests in the presence of humidity, whereas 100°C and 105°C have been used for “dry oven” accelerated aging tests. While testing in the presence of humidity seems logical in light of factors that are known to promote proton-catalyzed degradation (see earlier discussions), there is no guarantee that the results will be free of bias. High-temperature conditions can be expected to have an unequal effect on different chemical mechanisms.

The words “accelerated aging” also can refer to protocols using light exposure. For example, an ASTM method employs a xenon arc lamp (ASTM 2002b). Related tests have been used to evaluate the fading and yellowing of paper and printed items (Johnson 1989; Labelle and Breaul 2002; McGary *et al.* 2004; Fjellström *et al.* 2008). As already has been noted, light can affect some of the mechanisms by which paper degrades (Bukovský 2001; Bukovský and Kuka 2001; Rychly *et al.* 2006). Light exposure is of particular concern with respect to the yellowing or fading of paper and printed documents (McGary *et al.* 2004), an effect that sometimes is unrelated to acidity. However, deacidification with diethyl zinc has been found to increase the light-sensitivity of paper (Kelly and Williams 1981), and it would be worth carrying out related investigations for paper treated by other deacidification procedures.

Physical Testing

When comparing paper before and after accelerated aging, physical tests must be well chosen relative to the kinds of stresses likely to be encountered in the deacidified items. Among the tests that one could use for the before-and-after comparison, the MIT folding endurance test has been shown to be especially sensitive to aging phenomena (Darragh 1978; Wilson *et al.* 1981; Ramarao and Kumar 1986; Okayama *et al.* 1994, 1996b; Guerra *et al.* 1995; Pauk 1996; Porck 1996; Liers and Vogelsanger 1997; Moropoulou and Zervos 2003; Rychly *et al.* 2006; Zervos and Moropoulou 2006), although it may not track with other physical tests performed on the same test units. Tearing resistance (Anon. 2001) and tensile strength tests (Sundholm and Tahvanainen 2004) also have been used in such comparisons. Bursting tests, which are easy to perform, have also been used (Neevel 1995).

The fact that aged Brønsted-acidic paper often is most susceptible to failure in a folding mode provides evidence that embrittlement, rather than the loss of tensile strength, is the most critical issue (Roberson 1976). Figure 4 provides graphic evidence of this effect; micrographs show broken ends of fibers when old samples of acidic paper were folded. By contrast, the bottom center frame of Fig. 4 shows long, unbroken ends of fibers extending from the edge of a modern paper sheet that had been creased and then torn.

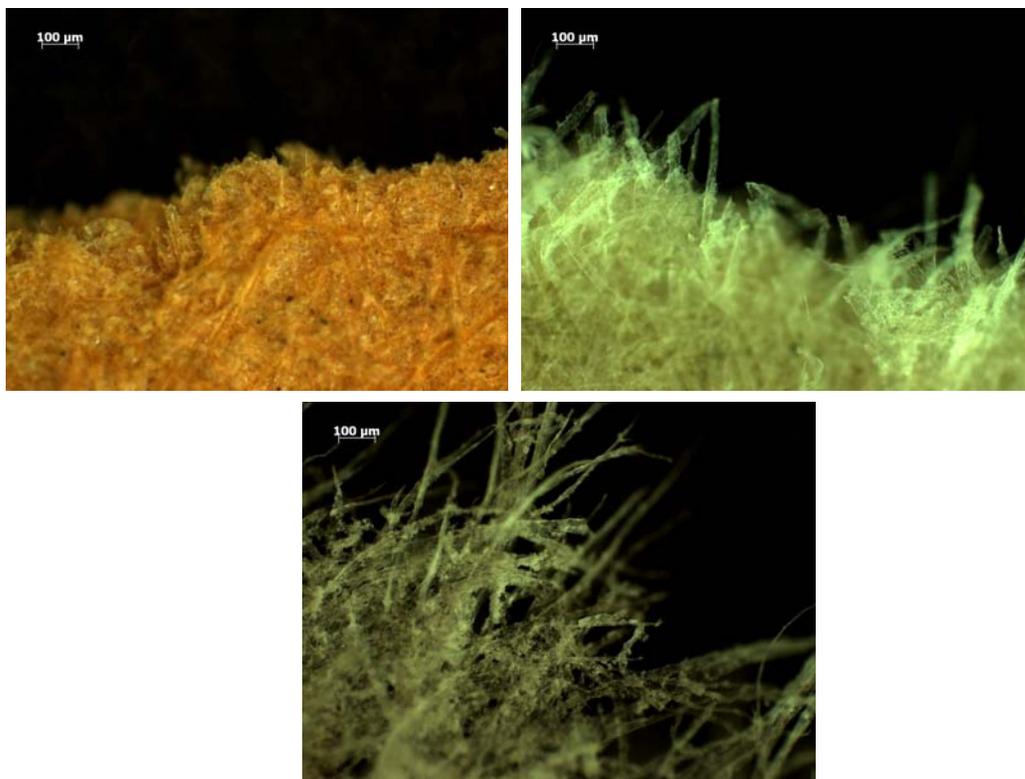


Figure 4. Photomicrographs of the broken or torn edges of paper, recorded under dark field illumination at 100x magnification, showing fiber length as a function of embrittlement. Left top: Acidic brittle paper from 1923 that fails with one fold; Right top: Acidic paper in slightly better condition from 1920 that fails with four folds (the standard library criteria for “brittle books”); Center, bottom: Current office paper torn along a creased fold

Effect of Brønsted Acidity on Drying-Induced Stiffening

It is well known that the drying of kraft fibers tends to reduce their flexibility and conformability in the wet state, interfering with their ability to bond together again in the preparation of recycled paper (Kato and Cameron 1999; Hubbe *et al.* 2007). The effect has been attributed to a virtually irreversible, progressive closure of submicroscopic pore spaces within the fiber walls. When the adjacent surfaces come together in the presence of sufficiently high moisture content, there can be a kind of healing process whereby coordinated hydrogen bonding between the surfaces essentially joins them together as one, as in a crystal. Results of a study by Lindström and Carlsson (1982) imply that such processes may become more important with decreasing pH, which is consistent with the

observed correlations of paper acidity with performance in folding endurance tests after accelerated aging. Presumably the same effects can occur during the aging of paper, especially if the humidity is relatively high or variable. Lindström (1990) listed crystallization as one of the likely causes of degradation of paper properties during aging, and he suggested that such processes may take place faster in cases where the molecular mass of the polysaccharides has been reduced by proton-catalyzed hydrolysis. Though the described effects are well known to papermakers, there is a need for research to determine the degree to which the same mechanisms contribute to paper's embrittlement during typical storage conditions.

Cellulose Degree of Polymerization (DP)

The molecular mass of cellulose, as determined by viscosity tests or gel permeation chromatography, is yet another way to quantify effects of paper deacidification (Eldin and Fahmy 1994; Kaminska and Burgess 1994; Liers and Vogelsanger 1997; Dupont *et al.* 2002; Kolar and Strlič 2004; Sundholm and Tahvanainen 2004; Zappalà and De Stefani 2005; Ipert *et al.* 2006; Sequeira *et al.* 2006; Henniges and Potthast 2008). Progress has been made in being able to evaluate cellulose DP even in samples that contain substantial amounts of lignin, as is the case for most newspaper and magazine samples (Kaminska 1997).

In principle, one may assume that a loss of molecular mass of the main component of the fibers should be correlated to a loss of strength. This is a difficult assumption to test experimentally, since conditions causing a reduction in cellulose DP are likely also to affect other fiber attributes, such as flexibility. Though some authors have observed correlations between reduced strength and reduced DP as a result of accelerated aging (Kaminska and Burgess 1994; Heywood 1997; Sundholm and Tahvanainen 2004; Ipert *et al.* 2006), some strength effects might also be attributed to an effect discussed earlier, a stiffening of the fibers during drying or storage that is promoted by low pH conditions (Weise 1998; Kato and Cameron 1999; Hubbe 2007). Further research is needed to clarify at what point a reduction in cellulose DP, by itself, can be expected to have a significant effect on paper strength, independent of other changes.

Changes in Paper's Appearance

When paper is exposed to conditions of accelerated aging, besides becoming more brittle, it also can lose brightness or become yellowed (Porck 1996). Such changes have been measured spectrophotometrically to evaluate deacidification programs (Pauk and van der Watering 1993).

Evidence of bleeding of inks or chromophores from the paper during implementation of a deacidification program can be found visually (Porck 1996). In the case of color illustrations in manuscripts there may be a danger of off-set onto the facing page (Scott 1987). Of the items that require deacidification, it is necessary to exclude those items that contain incompatible colorants (Scott 1987; Smith 1987; Sparks 1990). Banik (2005) noted that improper selection for deacidification can lead to bleeding of dyes, gross deformation, cockling, and the block-like sticking together of documents made from coated paper. Powdery deposits and damage due to air impingement are also

observed in some cases. During inspection of the treated paper, any planar deformation of the paper, such as cockling, would be an additional cause of complaint.

Odors

Odors are of particular concern in cases where paper has been treated with a solvent (Pauk and van de Watering 1993; Porck 1996). For instance, odor problems were noted during certain tests of items that had been subjected to the Battelle process (Havermans *et al.* 1996). Lienardy (1994) observed odor for one batch of items deacidified by the Wei T'oo process, but such issues were completely resolved when a second batch of treated books was evaluated.

Release of Monomers during Accelerated Aging

As noted by Banik (2005), tests of gases released from paper during accelerated aging can provide qualitative evidence of different types of degradative reactions. Evolution of furfural, which can be evaluated by gas chromatography and mass spectroscopy (GC/MS), provides evidence of hydrolysis of the polysaccharide components of paper. Likewise, acetic acid is a product of oxidative degradation, and its rate of evolution can be used to detect the rate of such reactions during accelerated aging. Strlič and coworkers (Strlič *et al.* 2009; Strlič 2009) have followed this line of thought, “smelling” old books to identify markers that indicate the composition of papers, and thereby targeting their likely inherent vices.

ASSOCIATED OR ALTERNATIVE TREATMENTS

In the course of carrying out deacidification treatments there can be opportunities to perform other useful procedures. If a printed item is being considered for aqueous deacidification, then it may make sense also to wash or repair that item at the same time (Shaw 1996; Kellerman 1999). A practice of disbinding and rebinding items, as a part of deacidification, can offer advantages associated with treatment of separate pages, which can be considerably easier to dry in the case of aqueous-based treatments. Some other treatments, such as the addition of strength-enhancing agents, have already been mentioned. Others are beneficial side effects of the various deacidification agents chosen. Though the most urgent goal of deacidification is often to arrest processes associated with aging, it is also possible to attempt further treatment, so that the strength and appearance of the item most closely resemble the original condition (Schwerdt 1989). The potential for associated treatments can factor into the institutional decision making process when choosing a particular method of deacidification.

Biocidal Effects of Deacidification Treatments

Smith (1987) noted that the fungicide bis(tributyl tin) oxide is compatible with the Wei T'oo process. Zappalà (1994) demonstrated simultaneous deacidification and antifungal treatment with calcium propionate. As mentioned before, Botti *et al.* (2006) noted that borax has anti-fungal effects. Rakotonirainy *et al.* (2008) evaluated the antifungal effects of aminoalkylalkoxysilane, which also functions as a strengthening

agent and as a source of alkalinity. Substantial reductions in fungal growth were observed.

Zerek (1997) found that most of the commonly used deacidification treatments were not very effective against most of the mold-forming organisms evaluated. In fact, only one combination of treatment and organism was effective, out of 300 investigated.

Strengthening Treatments

As no deacidification treatment can restore the internal fiber networking, in cases where the paper is very weak strengthening is required to retain the artifact. These operations tend to be time-consuming, and the resulting sheets no longer have nearly the same basis weight as the originals.

Polyester film encapsulation

A currently popular method of support for brittle paper is the use of inert polyester film. This is known as polyester film encapsulation. It is recommended that papers are deacidified prior to encapsulation (Kruth 1988). Double-sided tape, heat welds, and even sewing with thread have been used to secure the edges of polyester sheets for the purposes of encapsulation. Ultrasonic welding is another method, and it provides a strong inert bond of the film, which does not make fixed contact with the document. Due to static contact with the polyester, the housing enables flexibility and non-damaging movement of the document, which would not be possible otherwise. A document can be removed easily from this housing by simply cutting at the welds. This technique has been used for single-sheet material and for bound books. The encapsulated items can be bound, or the individual sheets can be stored in a box.

Lining

Lining using a thin lens (gossamer) tissue, Japanese tissue, or Korean papers have all been effective for supporting and thus strengthening weakened paper (Shaw 1996). A paper or tissue of appropriate tone, weight, and opacity is selected. In this process, the paper or tissue is coated with a wheat starch paste or starch-cellulose ether mix and used to line the entire back of the item, although at times both sides of the weakened paper are lined. Very fine Japanese tissues are available to achieve relatively large improvements in strength with a maximum of translucency. Alternatively, a very thin sheet can be prepared with a leaf caster, preferably using relatively long, refined bleached kraft fibers (Shaw 1996; Bansa 1998). Generally the original paper is dampened before applying the new thin, damp outer layers, thus allowing the whole structure to dry together in a symmetrical manner. The item is either dried flat under pressure as in Western conservation practices or dried under tension on a drying board (Karibari) as in Asian conservation practices (Webber 2006).

Leafcasting

Deacidification in conjunction with leafcasting is the preferred strategy, where available, for paper weakened by mold, or where significant losses and tears are present due to insect damage or other sources. Leafcasting is a mechanized method of papermaking wherein the weakened item is placed into the casting sink of a leafcaster.

Water is added into the sink with the document. Calculations based on the thickness of the paper needing to be infilled, the color and tone of the paper, and the area of loss are factored into making a slurry of paper pulp. The slurry is added to the casting sink. After manual agitation of the pulp, the leafcaster creates a suction from below the sink. The suction draws the water and paper fibers to the areas of loss, and within seconds the areas of damage in the sheet have been filled in. The treated sheet is then removed and placed on a suction table for drying. Just before it is completely dried, the treated sheet is sized either with methyl cellulose or gelatin, and the sheet will sometimes be pressed. One may then deacidify with a spray application. Alternatively, aqueous deacidification before the document is cast with magnesium bicarbonate or calcium bicarbonate is conducted, and the document is dried. Use of bicarbonate, rather than calcium hydroxide, will allow the alkaline reserve to be retained rather than washed out during the casting of the sheet (Mazel and Mowery 1986).

Paper splitting

Paper splitting is currently practiced in relatively few locations, and the focus has been on saving individual damaged items, *e.g.* pages damaged by iron gall ink or weakened by mold (Galinsky and Haberditzl 2004). A page is split through its vertical dimension (thickness), and an alkaline core of thin, strong, archival paper (typically a Japanese paper) is inserted and adhered between the two resulting halves (Porck 1996; Wächter *et al.* 1997). Paper splitting has been practiced for several centuries, although its application for paper strengthening was not seen until the 1930s when Barrow saw the value of inserting a stronger support sheet into a weakened sheet of paper (Brückle and Dambrogio 2000).

While various adhesives and methods may be used, the following is one example of a splitting technique (Brückle and Dambrogio 2000): The surface of the page to be split is faced on both surfaces with a synthetic material such as finely spun Reemay adhered using a protein-based adhesive, primarily gelatin. When the gelatin has dried sufficiently, these adhesive bonds to the faces of the sheet to be split are stronger than the cohesive bonds within the core of the paper itself. If the faced pages are uniformly pulled apart, the paper will split precisely down its vertical axis. This exposes the inner core of the sheet, into which a strengthening support is inserted and adhered with methyl cellulose (MC). The two halves of the split page are rejoined in full registration, with the new support inside. The item is dried under weight and allowed to cure for several days, after which it is immersed in a hot-water bath. As cellulose ethers do not dissolve in hot water, this bath will dissolve the gelatin from the facing pages, while leaving the core adhesive intact.

At the Zentrum für Buch-Erhaltung (ZfB) (Brückle and Dambrogio 2000) a specialized paper splitting machine has been developed. Documents are inserted in one end of this machine, where they are adhered to a support sheet (web), split, interleaved, and then pressed. The support sheet is then removed, and the completed document exits the machine. Unfortunately, as of 2010, this machine is being dismantled.

There is an alternative way to split paper that has been used in the laboratory; it is conceivable that it could also work in a production mode. Though this approach is known to paper scientists, there is no record of it having been practiced as a conservation

measure. It involves wetting individual sheets to a uniform moisture level and then passing each sheet under well-adjusted conditions of speed and temperature through a nip between two smooth metal rollers that are chilled below the freezing point of water (Parker and Mih 1964). The moistening weakens the hydrogen bonding between the constituent fibers of the paper, and localized freezing causes the paper surfaces to adhere to each of the rollers. Separation occurs at the not-yet-frozen core of the sheet. In principle, reassembly of the sheet with a new interleaved core can make use of the fact that hydrogen bonding among fibers in a sheet of paper is highly reversible (Hubbe 2006). By pressing the moist layers together and then drying the assembly under pressure, one can achieve bonding between the plies, as well as flatness. In practice it is expected that an adhesive, such as methylcellulose, would be needed to achieve suitable resistance to delamination. Furthermore, by selecting a suitable reinforcing ply, provided with a suitable reserve of alkalinity, the resulting structure can be expected to have improved resistance to proton-catalyzed degradation.

Lamination

Barrow (1965) was an early advocate of combining deacidification measures with lamination, especially in the case of weak paper articles. Some of the options that he used included simple lamination with cellulose acetate, or double-lamination—first applying a cellulose acetate layer, then applying a very thin tissue paper. The tissue paper provides strength and, if it is thin enough, does not have a major effect on the appearance. While this technique was employed in the past, cellulose acetate lamination is no longer recommended by conservators due to the adverse aging properties of the cellulose acetate materials (Bansa and Ishii 1997; Cope 2000). Zappalà *et al.* (2005) demonstrated the feasibility of laminating fragile papers onto a water-resistant sheet before their immersion into a deacidifying solution. Considerable flexibility was achieved by modifying the monomer composition of the lamination sheets.

Parylene deposition

As already discussed, certain strategies to strengthen paper are easily implemented as part of aqueous-based deacidification methods; however, a number of alternative treatments do not require the paper to be wet.

In the 1970s, Nova Tran, a subsidiary of Union Carbide, developed Parylene technology, a system that deposits a clear polymer conformal coating on the surface of paper (Humphrey 1986, 1990). The dry paper is treated with the vapors of diparaxylylene, a product of Union Carbide (Cunha 1989). The gas penetrates the fiber networks, depositing a smooth contouring coating of polymer along the fiber networks, which improves the flexibility of the paper, and thus fold endurance is enhanced. The material condenses onto the surfaces of paper and then polymerizes. The treatment has been shown to be effective in preserving pigmentation and structural elements in delicate specimens such as butterflies and other insects, and in increasing fold endurance in bound brittle pages of a book. The polymerized layer appears to coat the cellulosic material. Pilot tests of this process and their application to brittle books were spearheaded in the United States by Don Etherington. Initial costs of the process and the initial detectable deposit left on the page, along with the failure to successfully deliver a mass treatment in

the 1980s, resulted in preservation librarians abandoning this paper strengthening process. Studies continued in this area at the Canadian Conservation Institute in Ottawa (Grattan 2009).

Storage: Cool, Dry, Clean, Dark

In cases where one wants to avoid or defer deacidification measures, it is well known that degradation processes can be considerably decreased by controlling the temperature and humidity to relatively low values, *i.e.* “cold storage” (Carter 1988; McCormick-Goodhart and Wilhelm 2004; Smith 2004). Michalski (2002), in a paper by the same title demonstrates that one can “double the life for each five-degree drop,” and more than double the life for each halving of the relative humidity. Challenges with cold storage include access and staffing issues, where in the former case one must be careful not to damage the material by improper retrieval, causing condensate to form, and in the latter case specified temperatures for cold storage are inhospitable to workers for all but the briefest exposures.

A further measure that libraries can adopt to minimize the possibility of danger to their collections involves purification of the air (de Feber *et al.* 1998). For control of humidity, Lin *et al.* (2007) showed that it was possible to prepare “modified atmosphere and humidity packages,” consisting of selected salt hydrates. These agents were included within air-tight packaging of the items to be protected. Some of the agents were able to take up oxygen and release carbon dioxide, and resistance against mold organisms and foxing was also demonstrated.

Use Alkaline/Archival Paper in the First Place

It has been recommended that deacidification measures are most advantageously applied in the case of new items printed on Brønsted-acidic paper (Tse *et al.* 2002). The idea is to hold onto the original strength characteristics of the paper before significant degradation has had time to occur. However, as noted by Arnoult (1987), a puzzling issue is why deacidification programs should even be necessary in the first place. It would seem obvious, at least in retrospect, that it would be far cheaper and more convenient to simply manufacture the paper under alkaline or archival papermaking conditions (Cunha 1987). In fact, such a strategy is at least partly consistent with a major shift in the typical operating pH of paper machines that produce printing grades of paper (Hubbe 2005). Since the 1980s the majority of paper grades made with mineral fillers have been prepared with calcium carbonate, which serves to buffer the extract pH above about 7.5.

Reformatting and Digitalization

The final issue, digitalization, comes back to the detailed motivations that are being used to justify deacidification. If one merely needs a readable record of the contents of a book or other manuscript, rather than any intrinsic, historical, or evidentiary value, then some form of digital scanning may be satisfactory (McCrary 1990), as always, taking into account the associated costs. Prior to modern digitalization, many institutions relied upon microfilm for a photographic copy of brittle paper documents.

CONCLUDING REMARKS

The technologies cited in this review article evince considerable progress—but also considerable diversity—in the strategies that can be used to decrease the rate of decomposition of books, maps, manuscripts, and works of art on paper in libraries, museums, and archives. Despite this progress, numerous obstacles remain to be overcome, and additional research and collaboration between scientists and conservators is needed. While libraries, museums, and archives experience increased demand and use of electronic resources for access to information, conservators, scientists, and curators of paper-based collections continue to manage paper-based resources in recognition that many users continue to find a wealth of information contained in the object, as well as the pleasure and satisfaction of handling objects of knowledge. These artifacts of the human experience continue to be used extensively in our cultural institutions, and as such paper-based collections present rich and complex questions and challenges to scientists and conservators. At the center of this arena is the question of deacidification and the attendant issues. The authors hope that the information gathered together in this article can be helpful as paper technologists and conservators consider the next steps in terms of both research and implementation of deacidification programs.

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