Introduction

Paper is the primary material in many library and archive collections. Research by William J. Barrow and associates (The Barrow Book Collection) showed that paper became increasingly acidic and that its folding endurance significantly decreased in paper made toward the end of the 17th century. This problem became more pronounced in the 18th and 19th centuries, and continued unabated until alkaline papermaking became cost effective during the late 1980s. Although alkaline papermaking has become more economically attractive in many countries, libraries and archives throughout the world continue to receive collection materials printed on acidic paper.

The Library of Congress has a long history of pioneering and implementing state-of-the-art options for maximizing care and access for large collections. Prior to 1995, the Library researched, patented, and tested a number of processes that could be used for the mechanized en masse preventative care of acidic general and select special collection items. As part of that research, the Library provided the public with an extensive bibliography of the literature published prior to 1990 related to mass deacidification (Bibliography on Mass Deacidification).

In 1996, a contract with Preservation Technologies, L.P. enabled the Library to begin using the Bookkeeper® automated mass deacidification process to treat actual Library books for the first time rather than test books. In 2001, the Library presented Congress with its 35-year “One Generation” Mass Deacidification Plan to deacidify 8.5 million existing and newly acquired acidic books and 35 million sheets of unbound materials. In 2011, 10 years into the Plan, it is appropriate to evaluate the current state-of-the-art in mass deacidification. The evaluation includes this detailed, annotated bibliography that contains critical reviews of pertinent literature published primarily from 1990-2010, updating the previous Bibliography on Mass Deacidification.

Mass deacidification has become one cost-effective preservation option for large collections. It is used to neutralize acids and leave a reserve of alkalinity that continues to absorb acids either formed as the paper ages or as deposited from acidic pollutant gases such as sulfur dioxide (SO2) and nitrogen oxides (NOx). Modern commercial mass deacidification processes deposit the alkaline reserve using a variety of processes including aerosols for books, aqueous immersion for newspapers, and non-aqueous solvent immersion for books and manuscripts.

In addition to providing references specific to mass deacidification, this bibliography also provides background references that are useful for understanding the physicochemical properties of paper, methods for testing paper properties, and the fundamental chemistry of mass deacidification. References that were used during the critical review of the mass deacidification literature are also included and may predate the earlier Bibliography on Mass Deacidification. Each annotation begins with a description of the authors' credentials and concludes with a statement regarding whether or not the article was published in a journal that uses a fully anonymous peer review process as ascertained from information on the publishers’ websites. Comments in brackets [] are those of the author of this bibliography. The free and downloadable SCImago Research Group SJR: Scientific Journal Rankings database can be used to evaluate the quality of the journals.

All annotations reflect the analysis of the author and are not official statements of the Library of Congress. Comments and suggestions for improving this bibliography should be directed to the email address below.

Dr. Jeanette Adams, PhD Chemist
Library of Congress
Preservation Directorate
Binding and Collections Care Division
Washington, DC
www.loc.gov/rr/askalib/ask-preserv.html

The author of this bibliography thanks Cindy Connelly-Ryan, Jeanne Drewes, Joan Faltot, Judith Fiehler, Kenneth E. Harris, and Carole Zimmermann for their contributions during the preparation of this work.
Annotated Bibliography

2010


A scientist in the Binding and Collections Care Division of the Library of Congress reports the use of positive and negative ion direct analysis in real time mass spectrometry (DART-MS) to characterize Whatman #1 filter paper and 15 reference papers from the ASTM Paper Aging Research Program (Shahani et al., 2000, and Kaminska et al., 2000). The research presents a new method for studying the impact of mass deacidification on paper. Unique benchmark mass spectra were obtained from bleached northern hardwood kraft, bleached northern softwood kraft, hardwood- and softwood-bleached chemithermomechanical, and stone groundwood papers in real time without extractions, derivatizations, chromatographic separations, and time-, chemical-, and sample-consuming preparations. Microsamples as small as ~ 10 micrograms (μg), the approximate size of a printed period, were tweezed undetectably from the paper surface and analyzed. The method is highly sensitive and has the potential for being used to rapidly analyze changes in samples from natural and artificial aging studies conducted at lower temperatures. The article was published in an Elsevier journal with anonymous peer review.


The Heritage Science Postdoctoral Fellow (Baty), conservators (Maitland and Minter), and the Director of Conservation and Preservation (Jordan-Mowery) at the Sheridan Libraries, Johns Hopkins University, and a researcher in the Department of Forest Biomaterials, North Carolina State University (Hubbe), review an extensive list of literature (> 200) related to the deacidification of paper. Many of the citations presented in the article, and some of the original literature cited in the citations, are critically reviewed in this annotated bibliography. The article was published in an on-line journal with anonymous peer review.


This website provides links to a number of internet blogs about mass deacidification.


This website by the Nondestructive Testing (NDT) Resource Center of Iowa State University introduces tensile testing, which is important for understanding paper tensile strength before and after deacidification. A sample is stretched (strained) under a known load (stress), and the data is graphed as a stress-strain $xy$-plot in which $x$ is the amount of strain and $y$ is the amount of stress. The slope of the linear beginning elastic region of the plot is the Young’s (elastic) modulus. In this elastic region, no irreversible (plastic) deformation occurs, and release of the load results in the material returning to its original shape. A higher slope (modulus) is indicative of a stiffer material with a higher tensile strength that resists being stretched. The yield strength point is where the stretch finally starts increasing faster than the stress so that the next portion of the plot is curved with a decreased slope, indicative of the irreversible plastic deformation (elongation) of the material with slightly increasing loads. Brittle materials do not deform, they break near the end of the elastic portion of the curve, and they have a high tensile strength and modulus. More pliable (stretchy) viscoelastic materials stretch more with
increasing load and have a lower tensile strength and modulus. [Thus, brittle acidic paper generally has a high tensile strength even though it easily breaks under folding endurance tests.]

Popil, R. E. "Paper Testing Methods Lectures." Georgia Institute of Technology, Institute of Paper Science and Technology, 
http://ipst.gatech.edu/testing_services/paper_physical_testing/lectures.html.

A senior research scientist in the Department of Plasma Physics in the Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, GA, provides a series of lecture notes that describe physical property measurements of paper, which is relevant for understanding how the impact of mass deacidification on paper is evaluated. Of particular relevance are the notes on tensile strength, zero span tensile strength, tearing strength, folding endurance, brightness, and color. The lectures provide background and have detailed descriptions of the methods. Tensile strength (TS) in paper is primarily impacted by the strength of interfiber bonding that increases with fiber length, beating fibrillation, and increasing delignification. In particular, at low levels of interfiber bonding (as in newsprint paper), TS is most dependent on interfiber bond strength and fiber length. However, at higher levels of interfiber bonding (as in kraft chemical pulp paper), TS becomes increasingly more dependent on individual fiber strength. [Thus, TS of paper is impacted by a number of factors that vary among different types of paper and are impacted differently during treatment and/or aging.]


A faculty member in the Department of Library Science and Information Systems at the Technical Educational Institution of Athens, Greece, presents a comprehensive and critical analysis of the literature regarding natural and artificial aging of cellulose and paper, providing an excellent background for understanding paper aging and the need for deacidification. Acid hydrolysis is the main reaction at acidic pH, but at neutral and alkaline pH, oxidation, particularly catalyzed by transition metal ions, becomes important. Lignin causes yellowing but can stabilize cellulose against aging by acting as an antioxidant. Paper moisture content, not the relative humidity, is important to control in artificial aging. The degree of polymerization directly indicates degradation rates, whereas folding endurance, the most sensitive mechanical strength property, is only empirically related to reaction rates. Activation energies from Arrhenius studies reflect those from acid-catalyzed hydrolysis of cellulose, ~ 100-120 kJ mol⁻¹, but the pre-exponential A-factors are dependent on experimental conditions and the papers studied. Research issues that remain include determining quantitative relationships between natural and artificial aging; connecting reaction products to paper composition and aging conditions; elucidating mechanisms of alkaline paper degradation; determining the contribution of physical aging to the aging process; and developing non-destructive and miniaturizing existing techniques for characterizing paper. The article was published in a Nova Sciences Publishers book with anonymous peer review.

2009


The vice-president of the Centre Interrégional de Conservation du Livre (Interregional Center for the Conservation of the Book), a co-owner of a patent for using aminoalkylalkoxysilanes for deacidification, presents new data for using aminoalkylalkoxysilanes in mass deacidification (Cheradame 2001, 2003, 2004, 2005, 2006, and 2008). A critical analysis by the author of this bibliography of all data presented to date indicates the following: The solvents used in the process, hexamethyldisiloxane and tetramethylsilane, are extremely flammable, reactive, hazardous, and toxic. Aminoalkylalkoxysilanes and their byproducts are hazardous to humans and the environment. Folding endurance (FE) increased for one treated paper (Table II), but FE was previously shown to decrease for other treated papers (Cheradame, 2005 and 2006). Aminoalkylalkoxysilanes have not been shown to reproducibly simultaneously deacidify, deposit an alkaline reserve, and provide paper strengthening and protection
deacidification under normal storage conditions does not seem to occur (Cheradame, 2004). Treated
papers yellow (Cheradame, 2005) [probably from Maillard reactions between the amino group of the
silane and cellulose (Kelly, 1979; Tanaka, 1993; Painter, 2001; Bosetto, 2002; De La Orden, 2002;
Nursten, 2005; and Davidek, 2008)]. Treated papers need to be dried under vacuum or at a high
temperature. The impact of aminoalkylalkoxysilanes on printing inks has not yet been reported. The
article was published in a newsletter with no anonymous peer review.

Ebadi, A., J. S. S. Mohammadzadeh, and A. Khudiev. "What Is the Correct Form of BET Isotherm for

Researchers in the Chemical Engineering Department, Sahand University of Technology (Ebadi and
Khudiev) and the Chemical Engineering Department, University of Saskatchewan (Mohammadzadeh)
describe liquid-phase adsorption isotherms, which is background chemistry for the proposed use of
2008). Graphs show how to plot adsorption isotherms correctly and their general shapes. These
adsorption isotherms provide insight into the physical meaning of data for the adsorption of
aminoalkylalkoxysilanes on paper (Cheradame, 2004). The article was published in a Springer journal
with anonymous peer review.

Forum Bestandserhaltung. “Forum Bestandserhaltung-Massenneutralisierung (Conservation Forum-
Mass Neutralization).” http://www.uni-muenster.de/Forum-Bestandserhaltung/kons-
restaurierung/neutral.html (accessed October 5, 2009).

Links to many European conservation projects including mass deacidification are contained on this
web-based conservation project forum sponsored by the Deutsche Forschungsgemeinschaft (DFG:
German Research Foundation). The links are primarily to on-line, non-English, HTML and PDF
documents.

http://www.rsc.org/Education/EiC/issues/2009Sept/SonochemistryBeyondSynthesis.asp (accessed
January 29, 2010).

A Professor of Chemistry and the Director of the Sonochemistry Centre, Coventry University, UK,
introduce sonication, which is related to the Kundrot patent (Kundrot, 1999) that uses sonication of
metal oxide particles in a gas-solid fluidized bed to deacidify papers and books. Sonication in systems
that involve liquids can be highly damaging because of the phenomenon of cavituation (microbubble
formation and implosive collapse) that can create temperatures as high as 5000 K, pressures as high
as 2000 atm, and intense shock waves in the microenvironment of the bubble. Sonication in a gas-
solid fluidized bed may not damage the cellulose in paper as might aqueous sonication, but the impact
of sonication from a gas-solid fluidized bed on cellulose in paper has not been reported. The article
was published in a RSC (Royal Society of Chemistry) journal with anonymous peer review.


An Association of Research Libraries (ARL) Visiting Program Officer describes the preservation
activities of ARL libraries, which include mass deacidification, creating digital surrogates, developing
digital repositories, and others. Digitization is described as being both for access and for preservation
with the understanding that the digital surrogates must in themselves be preserved, metadata must be
produced and maintained, and search mechanisms must be developed. Mass deacidification is
described as being valuable for printed works that cannot be reformatted due to copyright restrictions
and/or that have enduring value in their original format, and for preserving unique archival materials. A
study group indicated that there is still need for reliable and sustained research on paper chemistry, the
strengthening and stabilization impact of deacidification, and its long-term effects on materials.
Collaborative strategies between libraries in both digitization and mass deacidification are
recommended to reduce duplication of effort and to provide for shared storage. The article was
This technical newsletter from Polymathic Analytical Labs describes how direct substantive dyes such as Brilliant Yellow (pH indicating dye) are hydrogen bonded to cellulose via the dye's phenolic groups. This is relevant for understanding why using the color change of Brilliant Yellow dye as a test of the deacidification efficacy of the Bookkeeper® processes is not a valid indicator of pH (Kidder et al., 1998). The strength of the hydrogen bonding is so strong that an aqueous alkaline solution of pyridine (an organic base) must be used to extract the dye from cellulose. The alkaline solution deprotonates (ionizes and dissociates) the phenolic groups, breaking the hydrogen bonding to produce dye anions that are then solvated by water. It is only at this point that the dye would be able to change color from yellow to orange indicating the presence of alkalinity. [This is why Brilliant Yellow and similar dyes absorbed onto paper prior to a non-aqueous deacidification treatment would not be expected to change color to indicate the extent of deacidification until enough moisture was present from humidification to solvate the dye and disrupt the hydrogen bonding to the cellulose.] The article was published as a company bulletin.


Staff (Ramin, Andres, Reist, and Wälchli) at Nitrochemie Wimmis AG, the company that provides the Papersave® mass deacidification process, and the Head of Paper Deacidification (Blüher) at the Swiss National Library describe results from work that was presented at the Xth Internationale Arbeitsgemeinschaft der Archiv- Bibliotheks- und Graphikrestauratoren [International Association of Archive, Book and Paper Conservators (IADA)] Congress at Vienna in September 2007. The purpose of the study was to compare three mass deacidification processes in terms of the influence of artificial aging on the physicochemical and mechanical properties of papers. Papers treated with aqueous calcium and magnesium carbonate and with the Papersave® process were artificially aged for 150 days, but papers treated with the Bookkeeper® and Booksaver® processes were only aged for 48 days. However, papers treated with the aqueous carbonates and with Bookkeeper® were treated as single sheets, whereas papers treated with Papersave® and Booksaver® were treated in stacks. [As no two paper treatments and aging conditions were the same, comparative conclusions are difficult to draw.] The article was published in an IADA journal with anonymous peer review.


Researchers at the Art Conservation Research Center at Carnegie Mellon University studied effects of aqueous calcium hydroxide treatment on oxidized paper. This is relevant to the effect of mass deacidification on the long-term stability of older papers. Measurements of the degree of polymerization (DP) of the cellulose showed that baths at pH 8.5 [similar to the pH of papers after mass deacidification] had no deleterious effect on the DP of papers oxidized with UV-A or hydrogen peroxide. Baths at pH 10.0 [a high alkalinity not routinely obtained during mass deacidification] had minimal to no effect on the DP of papers oxidized with UV-A or hydrogen peroxide, which was interpreted to mean that oxidation occurred on the terminal ends of the cellulose chains as was believed to occur during natural aging. Baths at pH 12.5 [higher than obtainable via mass deacidification] had negative effects on all oxidized samples. For samples oxidized with sodium periodate, however, all alkaline pH baths had a negative impact, which was interpreted to mean that oxidation occurred throughout the cellulose chains, not simply at the ends. The article was published in an AIC (American Institute for Conservation) journal with anonymous peer review.
2008


Staff (Andres, Reist, Vogelsanger, and Wälchli) at Nitrochemie Wimmis AG, the company that provides Papersave®, and the Heads of Paper Deacidification (Blüher) and the Conservation Department (Grossenbacher) of the Swiss National Library conducted artificial aging experiments to test model acidic papers that were either mass deacidified using different concentrations of the Papersave® Swiss process or were deacidified as single sheets using immersion in aqueous calcium and magnesium bicarbonate. During artificial aging, the pH and alkaline reserve of the papers decreased, the color darkened/yellowed, and the limiting viscosity value that reflected the degree of polymerization of cellulose decreased, but the decreases were dependent on concentration. Aqueous, single-sheet, deacidification gave the best results. Optimum treatment concentrations in reference to the results are discussed. The article was published in a journal with no anonymous peer review.


Researchers at the Russian State Library, Moscow, Russian Federation, describe mass deacidifying acidic groundwood papers using the Neschen (Bückeburg) process. Artificial hydrothermal aging of samples was followed by determination of pH, tear resistance, tensile strength, and elemental analysis of the used treatment solution. The aqueous deacidification solution, which was composed of magnesium bicarbonate, polyionic agents, and methylcellulose, began at pH 7.2 and was colorless. After treatment, its color changed to brown because it contained colored degradation products that were washed from the samples. The used solution also contained high amounts of iron, calcium, manganese, copper, lead, zinc, chromium, and aluminum. Although the pH of the used solution was more alkaline (pH 9), it was not as effective at deacidifying paper as a fresh solution at pH 7.2. [This is probably because after use, the soluble magnesium bicarbonate changed into insoluble magnesium carbonate and/or insoluble metal hydroxides, the latter which are more basic species than magnesium bicarbonate but apparently not as effective at deacidification in the process.] Carbon dioxide was periodically added to the solution to regenerate the soluble magnesium bicarbonate and bring the pH back down to 7.2. The article was published in conference proceedings with no anonymous peer review.


Researchers at Nestle Product Technology Centre Orbe (Davidek, Gouézec, and Blank) and the Nestlé Research Center (Devaud) in Switzerland show that acetic acid is a major product in the Maillard reaction between glycine and xylose, in direct analogy to Maillard reactions that occur with hexoses at neutral and alkaline pH, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006, and 2008). An alkaline pH was found to particularly catalyze the reaction. [The amino groups of aminoalkylalkoxysilanes are similarly expected to undergo Maillard reactions with carbohydrates and other components of paper, reactions that might be catalyzed by an alkaline reserve present in the paper and result in the formation of acetic acid.] The article was published in conference proceedings with no anonymous peer review.


Researchers in the Department of Chemistry, the Institute for Advanced Materials, Nanoscience and
Technology, and the NSF Science and Technology Center for Environmentally Responsible Solvents and Processes, University of North Carolina at Chapel Hill (Guo and DeSimone), Fluoroscience LLC (Resnick), and the Department of Chemical and Biomolecular Engineering, North Carolina State University (Efimenko and Genzer) provide a concise description of the biopersistence and toxicity of long-chain perfluorinated acids, which is relevant for evaluating the environmental impact of the surfactant used in the Bookkeeper® deacidification process. Of most concern is perfluorooctanoic acid, primarily formed by oxidative degradation of stain- and grease-resistant coatings on textiles, carpets, and paper. Alternatives that contain carbon chains shorter than C5 do not bioaccumulate and are not persistent. [The surfactant used in Bookkeeper® to help keep the magnesium oxide particles dispersed is an anionic perfluoropolyether acid that should be more biodegradable because of its ether linkages, and whose biodegradation products should result in short-chain perfluorinated compounds that should not bioaccumulate and should not be biopersistent (Leiner and Kifer, 1993; Leiner et al., 1998; Leiner et al., 2000; Kissa, 2001; Zumbühl and Wulfert, 2001; and Järnberg and van Bavel, 2006).] This article was published in an ACS (American Chemical Society) journal with anonymous peer review.


Researchers at the Slovak National Archives (Hanus); the Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology (Bakoš, Vrška, Jablonský, Katuščák, Holubkova); the Slovak National Library (Bajziková and Bukovský); and the Polymer Institute, Slovak Academy of Sciences (Rychlý) describe the Kniha project, whose aim is to support education, research, and industry in conservation science, technology, and industry in Slovakia. One set of results from the project was from testing Papersave®, Libertec®, and CSC Booksaver® deacidification processes by evaluating the impact of deacidification on folding endurance after artificial aging. Of the above three deacidification methods, which were the only ones tested using identical testing conditions, only Papersave® and Libertec® met the criteria for stability (a three-time enhancement of folding endurance after treatment). The article was published in conference proceedings with no anonymous peer review.


Researchers at TNO Built Environment & Geosciences, Delft, Netherlands, give brief descriptions of mass deacidification and/or paper strengthening processes that are no longer commercially available. These include diethylzinc (DEZ), Wei T'o®, FMC-Lithco-MG3, graft-copolymerization, and the first "Battelle" version of Papersave®. The DEZ process is described as being the most promising but the most complicated and dangerous. Wei T'o® caused cockling, yellowing, white residue, discolorations, and paper weakening. The FMC process using heptane as solvent was not successful. Graft-copolymerization involved using gamma rays to irreversibly polymerize and bind acrylic and methacrylic monomers to the cellulose in paper. The first "Battelle" version of Papersave® used Freon®, but this was changed to hexamethyldisiloxane in accord with the Montreal Protocol. It was concluded that most of the processes developed were successful in neutralizing acids in paper, but more is needed (environmental friendliness, simplicity). The article was published in conference proceedings with no anonymous peer review.

Scientists in the Department of Printing Arts Technology and Photochemistry IPM (Havlínová, Reháková, Petrovičová, and Jančovičová), Bratislava, Slovakia, and the National Archive in Prague (Ďurovič), Czech Republic, investigated the impact of relative humidity (RH) and paper pH on arylmethane dyes after deacidification using the CSC Booksaver® process. Samples of the original acidic groundwood paper and the deacidified paper were treated with acid green, methylene blue, and basic red dyes and then artificially hydrothermally aged. For acid green and methylene blue, deacidification resulted in better color retention (less fading to gray) at all RH values. However, for basic red, deacidification resulted in significantly worse color retention (more fading to gray) at all RH values. The overall trends in decreasing stability were basic red/acidic paper > acid green/basic paper > methylene blue/basic paper > acid green/acid paper > methylene blue/acid paper > basic red/basic paper. Which of the numerous basic red dyes was used in the study was not stated, and the chemistry involved in the fading reactions was not described. The article was published in conference proceedings with no anonymous peer review.


Researchers at the Institute of Polymer Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, performed artificial aging experiments to test acidic newsprint papers that had been deacidified using the CSC Booksaver® process. A comparison of breaking length and folding endurance between controls and deacidified papers showed that the process did not positively impact strength after aging to an extent that the process would meet international deacidification efficacy standards. A useful bar chart is presented that shows the results in relation to results from a large number of other tested deacidification processes. The article was published in a Faculty of Chemical and Food Technology, Slovak University of Technology, journal.


Researchers at the Institute of Polymer Materials, Slovak University of Technology (Holúbková, Jablonský, and Katuščák), the Slovak National Library (Bajzíková and Bukovský), the Slovak National Archives (Hanus), and the Polymer Institute of the Slovak Academy of Sciences (Rychlý), Slovak Republic, report results from hydrothermal artificial aging of newsprint papers mass deacidified using the Libertec® process, which uses calcium carbonate and magnesium oxide as an aerosol dust. The process increased the relative lifetimes of the samples, significantly improved the mechanical strength, was not very expensive, was very ecological, and was safe in terms of danger of fire and health hazards. The article was published in conference proceedings with no anonymous peer review.


Researchers in the Department of Chemical Technology of Wood, Pulp and Paper (Jablonský and Tiño) and the Department of Analytical Chemistry (Hroboňová) at the Slovak University of Technology, Bratislava, Slovak Republic, describe results from hydrothermal artificial aging of newsprint paper, which is relevant for understanding effects of aging on paper. Aged paper samples were extracted with water, and then formic and acetic acids were quantitated by using ion chromatography (IC). Paper yellowing was analyzed by using colorimetry. The concentration of formic acid was not related to either the time of aging or the amount of yellowing. However, the concentration of acetic acid correlated well with the time of aging, but less so with the amount of yellowing. It was noted that using the physical
property of color change as an indicator of chemical degradation either is not particularly reliable, at least in terms of formation of formic and acetic acids, or the total concentrations of the volatile acids formed during aging were not measured [i.e., a portion of the acids, particularly formic, perhaps were volatilized and/or absorbed by the plastic bags in which the samples were aged]. Other researchers previously showed that yellowing is not a good indicator of the degree of degradation of cellulose (Havermans, 1995). The article was published in conference proceedings with no anonymous peer review.


Researchers at the Mid Sweden University, Sundsvall, Sweden, report results from high-temperature (120-180 °C) artificial aging of high-cellulose papers impregnated with magnesium Mg(II), calcium Ca(II), and iron Fe(III) chlorides. Dry aging at 180 °C caused cotton sheets at starting pH 5 to degrade more when impregnated with either Mg(II) or Ca(II) than with Fe(III). For sheets at starting pH 3, 5, or 8, Mg(II)-treated sheets degraded more than untreated sheets. The conclusion was that Mg(II) was a Lewis acid catalyst for cellulose degradation. [However, the concentration of metallic and non-metallic impurities, including strong Lewis acids and boron salts known to be present in commercial anhydrous Mg(II) and Ca(II) chloride salts, was not addressed. Such impurities, if present, could have accounted for the degradation, particularly because high levels of the salts were used in the experiments. Final paper pH was not determined, but under these extremely high temperature conditions, oxidation, not Lewis-acid catalyzed degradation per se, might have been the predominant reaction. Perhaps this is why the authors’ conclusion cannot be reconciled with the fact that Fe(III) is a significantly stronger Lewis acid than Mg(II) and Ca(II), but the data as interpreted by the authors would indicate the opposite.] The article was published in a journal with anonymous peer review.


Researchers at the University of Ljubljana (Mencigar, Trafela, Mozetič, and Kočar) and the National and University Library (Kolar), Ljubljana, Slovenia, and the Centre for Sustainable Heritage, University College London, UK (Strlič), investigated the concentration of rosin acids, which are contained in alum-rosin sizing, through time and their effects on the pH of paper. This is relevant for understanding the source of acidity in and consequent degradation of alum-rosin sized papers. Rosin acids were extracted and then determined by using liquid chromatography-mass spectrometry. There was an almost Gaussian distribution of rosin acid concentration from years 1850 to ~ 2000, and it maximized approximately at 1900. Between 1900 and 2000, rosin acids decreased slowly, but modern papers continue to contain rosin acids if they are manufactured from groundwood fibers. The pH decreased as rosin acid concentration increased unless papers had been deacidified or if they were modern alkaline papers that also contained high levels of rosin from groundwood. [In analogy to trimethylacetic acid, rosin acids are predicted to have pKa values of ~ 5 (TC NES Subgroup, 2008), so they, as acetic acid (pKa ~ 5) and formic acid (pKa ~ 4), can be expected to contribute to the acidity of paper.] The article was published in conference proceedings with no anonymous peer review.


A study group comprised of a Columbia University librarian (Neal), the former head of preservation at Stanford University (Brooks), the head of preservation at New York University (DeStefano), a Yale University librarian (Prochaska), and a senior advisor to the Mellon Foundation (Rütimann) describes results from their task to gather information about current deacidification practices and experiences and to investigate the CSC Booksaver® process. No information about the Booksaver® process was given,
but can be found in other articles in this annotated bibliography (Hanus, 2008; Rhys-Lewis, 2003; Meese, 2005; Blüher, 2001). Two important conclusions were: (1) there is a need for more reliable and sustained research on paper chemistry, the stabilizing and strengthening impact of mass deacidification, and its long-term effects on materials, and (2) libraries still receive a large amount of material that requires deacidification. The article was published in a magazine with no anonymous peer review.


Conservators at the Russian State Library, Moscow, Russian Federation, describe the restoration of acidic newspapers by using the aqueous Neschen (Bückeburg) process followed by final treatment with adhesive paper films. The first stage of the Neschen process involved a bath of aqueous pH 7.2 magnesium Mg(II) bicarbonate, methylcellulose, and Rewin®/Mesitol® fixatives, the latter which prevented water-unstable inks from migrating. The second heating stage evaporated the water, leaving Mg(II) bicarbonate that was converted into Mg(II) carbonate, and methylcellulose that reinforced the paper. The problems with the treatment included an increase in yellowing, the need to treat fragile sheets by hand, traces of the conveyor belt grid on some papers, and some construction difficulties. The final restorative treatment involved pressing the newspapers and applying a final adhesive paper film. The film was either Neschen Filmoplast® P (a short-fiber, transparent, acid-free paper with a non-yellowing, neutral adhesive, buffered with calcium Ca(II) carbonate) or Filmoplast® R (a transparent, long-fiber, Japanese, acid-free paper, coated with an acrylic adhesive). After treatment, the newspapers were stored, and only facsimiles were available for readers without special permission. The article was published in conference proceedings with no anonymous peer review.


Paper specialists at PTS used data from the literature and developed a simple model for illustrating the impact of different parameters on the lifetime of high-cellulose paper, which is relevant for understanding the aging of paper and the need for deacidification. Cellulose fibers age because the cellulose chains become shorter, reducing their degree of polymerization (DP). Degradation primarily occurs in the amorphous regions of the fibers, which contain free moisture, as opposed to the crystalline regions, which are anhydrous. Folding endurance is the first, and tear strength the second, mechanical parameter that is impacted by degradation because they both primarily reflect the strength of single fibers. The model shows that a five degree drop in temperature increases relative paper lifetime by 100%; decreasing the moisture content from 8% to 6% increases lifetime by 30%; increasing the pH from 5 to 6 increases lifetime by 30%, but the improvement levels above pH 7; and increasing the starting DP from 560 to 1150 increases lifetime by 25%. The moisture content is inversely related to temperature. The model indicates that if other factors, such as light and molds, were minimized, and the papers were alkaline, the aging behavior would be controlled by temperature (a significant exponential influence), the initial DP, and the moisture content. The article was published as a report with no anonymous peer review.


The vice-president (Cheradádame) and managing director (Ipert) of the Centre Interrégional de Conservation du Livre (Interregional Center for the Conservation of the Book), co-owners of a patent for using aminoalkylalkoxysilanes for deacidification, and researchers from CNRS (Rakotonirainy and Dupont) studied the use of aminoalkylalkoxysilanes as fungicides for paper. Hexamethyldisiloxane and
tetramethylsilane, both highly flammable and toxic, were used as solvents instead of ethanol as used in
previous studies (Cheradame, 2003, 2004, 2005, and 2006). The greatest fungicidal activity was
reported for the silane abbreviated "AMDES", but the effect of artificial aging on the fungicidal activity of
this silane was not presented. Instead, the effect of artificial aging on the fungicidal activity of a
different silane, "ADBTMS", was instead presented. This makes it difficult to compare the results and
draw comparative conclusions. Data reported in Table 4 are not consistent with data in Table 1: Less
fungal growth is reported for paper 1 treated with 5.6% ADBTMS in Table 4, but more growth is
reported for the same paper treated with a higher concentration of the silane (Table 1), opposite to what
would have been expected if the silane had fungicidal activity. The article was published in an Elsevier
journal with anonymous peer review.


Researchers in the Department of Chemical Engineering of Aristotle University of Thessaloniki studied
the UV-light artificial aging of paper sheets that had been deacidified by immersion in dispersions of
0.4-1.5 micron-size particles of calcium and magnesium hydroxides in alcohols. The paper samples
were alkaline office copy paper and Whatman filter paper. One unsurprising trend was that changes in
yellowness index and tensile strength before and after aging were significantly different for the two
different types of papers. The micron-sized particles are described as "nanoparticles" even though
"nanoparticles" range in size from 1-100 nm, which is significantly smaller than the size of the particles
described in the article. The data are not complete enough to permit conclusions to be drawn regarding
relative impact of particle size on stability. Controls that include typical particle sizes and typical
deacidification solutions were not studied so the data cannot be compared to data from other
deacidification processes. The article was published in a journal with no anonymous peer review.

Ljubljana, SI: Faculty of Chemistry and Chemical Technology, 2008.

Researchers at the Centre for Sustainable Heritage, University College London (Strlič); the University
of Ljubljana (Cigič) and the National and University Library (Kolar), Slovenia; and the Nationaal Archief,
The Hague, The Netherlands (Steemers) describe results from sampling volatile organic compounds
emitted from paper during aging. Many of the compounds can initiate or accelerate degradation of
cellulose, and they are most strongly emitted from acidic paper. The data suggest that deacidification
reagents will serve not only to deacidify paper but to neutralize and absorb volatile acids and other
harmful compounds that are admitted during degradation of paper. This function will also help reduce
cross-infection of other materials in storage facilities. The article was published in conference
proceedings with no anonymous peer review.

TC NES Subgroup on Identification of PBT and VPVP Substances. *Results of the Evaluation of the
PBT/VPVB Properties of Tall-Oil Rosin*. European Commission Joint Research Centre (JRC),
European Chemicals Bureau (ECB).
(accessed November 5, 2010).

The European Chemicals Bureau (ECB) Technical Committee on New and Existing Substances (TC
NES) reports their evaluation of the rosin acids in tall oil as Persistent, Bioaccumulating, and Toxic
substances (PBTs) and very Persistent and very Bioaccumulating substances (vPvBs). The data are
relevant because rosin acids are found in paper that has been sized using alum-rosin sizing and in
paper that contains stoneground wood (Adams, 2011), and they contribute to the acidity of paper
(Mencigar et al., 2008). The report provides structures, Chemical Abstracts Service (CAS) numbers,
and other data regarding their physical and chemical properties. The pKa values for the rosin acids
were predicted to be ~ 5 using a software algorithm, which is consistent with expectations for a
carboxylic acid functional group. The article was published as a report with peer review.


Researchers from the Faculty of Chemistry, Warsaw University (Wagner and Bulska) and the Poland National Library (Sobucki) studied the distribution of magnesium Mg(II) in sheets from early 20th century books that had been deacidified using either the Neschen (Bückeburg) or the CSC Booksaver® processes. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was the analytical technique. The distributions for both deacidification processes were highly variable. It is not possible to reliably compare the Mg(II) distributions for the two processes because the books that were deacidified and analyzed were not duplicates, the accuracy and precision of the analytical method itself were not given, the actual Mg(II) distributions were not shown, and the means and the modes of the distributions were not given. The article was published in an Elsevier journal with anonymous peer review.

2007


Researchers at the National and University Library of Slovenia (Kolar, Balažic, Habicht, and Smodis) and the University of Ljubljana (Strlič) derived stabilization factors for deacidification and cold storage from Arrhenius artificial hydrothermal aging experiments using papers deacidified with Bookkeeper®. However, the linear regression equations presented appear to have slopes that are an order of magnitude too large to provide activation energies (E_a) close to the E_a for paper/cellulose depolymerization, which should be ~ 100-120 kJ mol⁻¹ (Zervos, 2010). [Replotting the data and recalculating give values for E_a that appear to be too small (~ 90-95 kJ mol⁻¹), and the stabilization factor for deacidification and cold storage appears to be 18 instead of 30.] The experiments were conducted at constant relative humidity (RH) instead of constant paper moisture content, the latter being the variable that needs to be held constant in Arrhenius experiments (Shahani et al., 2000; Kaminska et al., 2000; PTS, 2008; Zervos, 2010). It is not clear whether the reduced reaction rates for deacidified papers are a result of deacidification per se or simply because deacidification reduces the moisture content in treated papers compared to the controls, which would reduce the reaction rates. The article was published in conference proceedings with no anonymous peer review.


Scientists at the MATAR Research Centre, London College of Communication, University of the Arts, London, UK, describe how aqueous sonication of recycled pulps de-inks paper. This is related to the Kundrot patent (Kundrot, 1999) that uses sonication of metal oxide particles in a gas-solid fluidized bed to deacidify papers and books. Sonication in a gas-solid fluidized bed may not de-ink paper as does aqueous sonication, but the impact of sonication from a gas-solid fluidized bed on inks in printed paper has not been reported. The article was published in an Emerald journal with anonymous peer review.


A researcher from the Department of Chemistry & Biochemistry, Florida State University, using equipment in the Preservation Research & Testing Division, Library of Congress, describes the effect of sonication of cellulose in water, which results in its degradation. This is related to the Kundrot patent (Kundrot, 1999) that uses sonication of metal oxide particles in a gas-solid fluidized bed to deacidify
papers and books. Sonication in a gas-solid fluidized bed may not degrade the cellulose in paper as does aqueous sonication, but the impact of sonication from a gas-solid fluidized bed on cellulose in paper has not been reported. The article was published in an ACS (American Chemical Society) journal with anonymous peer review.

2006


Scientists at the Helsinki University of Technology, Laboratory of Physics (Alava) and KCL Science and Consulting (Niskanen), Finland, discuss the rheological properties of paper, which is relevant for understanding how paper ages and the physicochemical meaning of tensile strength. The elastic modulus (stiffness) and tensile strength of paper are smaller than those of individual fibers because paper is porous and the fibers are randomly oriented. Moisture decreases the elastic modulus and tensile strength due to softening of amorphous components of the fiber wall. In dry conditions, paper is brittle and hard with a high modulus and tensile strength, but at high relative humidity (RH), paper is ductile and soft with a low modulus and tensile strength. Both the elastic modulus and tensile strength of paper increase with an increase in the rate at which the paper is strained in tensile tests. Paper is generally stiff and brittle at high strain rates, but soft and ductile at low strain rates. Macroscopic paper fracture is primarily a result of plastic (inelastic, irreversible) elongation (deformation) of fibers caused by microfibrils sliding relative to each other breaking interfiber bonds so that fibers are pulled out of the network at the fracture, not broken. This is why tensile strength is primarily a measurement of interfiber bonding, not individual fiber strength. Water absorption causes deformations, but the deformations are elastic for small amounts of water. With increasing amounts of water, however, the stress may exceed the yield limit and cause plastic, irreversible deformations. The article was published in an Institute of Physics (IOP) Publishing journal with anonymous peer review.


A scientist in Research and Development at Nitrochemie Wimmis AG, the company that provides Papersave®, describes the disinfecting and growth-inhibiting effect of the Papersave® Swiss process on mold. A useful table of the different types of molds that grow on paper is given. Mold growth on paper that had been contaminated with mold spores prior to deacidification either was not significantly impacted or was not decreased by deacidification if the papers were incubated on dextrose agar, a nutrient medium with an acidic pH. This showed that the deacidification process did not disinfect, or kill, the spores. However, when the treated contaminated papers were instead aged at 28 °C and 75% relative humidity with no addition of dextrose agar, the treatment was shown to reduce fungal growth. The reduction in growth was less when the paper had been sized with albumen, a source of nutrients for mold growth. The alkaline pH of the treated papers was credited for the inhibition of growth on the treated papers. The article was published in conference proceedings with no anonymous peer review.


The president and founder of Gelest, Inc. introduces the chemistry of silanes and aminoalkoxysilanes, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006, and 2008). In particular, methoxysilanes hydrolyze seven times faster than ethoxysilanes, and acidic and basic pH favors hydrolysis and condensation to form polymeric coatings. [Thus, aminoalkylalkoxysilanes used for deacidification reagents can be expected to form polymeric coatings on paper.] A useful equation is
given for silane needed to obtain a minimum uniform multilayer coverage on a surface, which can be used to better understand the absorption data provided in Cheradame (2004).


The president and founder of Gelest, Inc. introduces the chemistry of alkoxysilanes, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006, and 2008). Ambient moisture converts the alkoxy groups to silanols that self-react to form polymer films. Bonds between the polymer and a substrate [such as paper] can then be formed by applying either heat or vacuum to remove water. [Trialkoxysilanes such as used in the Cheradame articles, are expected to bulk deposit from solution onto the paper substrate as polymeric films because there is water present in the paper. This differs from monolayer coverage that requires pre-drying the substrate and performing the reaction under anhydrous conditions, which is not the procedure in the Cheradame articles].


Researchers at the Dipartimento di Chimica and Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase of the Università degli Studi di Firenze review the synthesis and use of nanoparticles (particles that are less than 100 nanometers (nm) in size) of alkaline earth oxides, hydroxides, and carbonates in art conservation and their possible use in mass deacidification of paper. A number of references for the use of dispersions of calcium hydroxide nanoparticles in non-aqueous solvents for repair of porous painted surfaces are given. The deacidification chemistry and pros and cons of diethylzinc (DEZ), Wei T'o®, Papersave® (Battelle), and Bookkeeper® are summarized, and it is suggested that nano-particle dispersions of magnesium and calcium hydroxides in alcohols could be alternatives. The article was published in a RSC (Royal Society of Chemistry) journal with anonymous peer review.


The Head of the Training Programme (Banik) and a researcher (Doering) at the Staatliche Akademie der Bildenden Künste Stuttgart Studiengang Restaurierund und Konservierung von Graphik, Archiv- und Bibliotheksgut, and the Head of the Conservation Department at the Universtitätsbibliothek Marburg (Hähner) primarily describe analytical tools developed to determine the efficacy of mass deacidification. Solid-phase micro-extraction (SPME) and gas chromatography-mass spectrometry (GC-MS) were used to compare the levels of furfural (from acid hydrolysis) vs. acetic acid (from oxidation) after deacidification using the Papersave®, Neschen (Bückeburg), Bookkeeper®, and Libertec® processes. Analytical data from a yet-to-be-publicly available PhD dissertation was referenced. The liquid-phase deacidification processes (i.e., all but Libertec®) were successful in extracting pre-formed acetic acid from the papers, but no process was able to prevent acetic acid from forming during artificial aging. The ability of Papersave® to enhance the stability of paper depended on treatment plant. Models were presented for collection selection criteria, workflow, quality management, and risk indices for different processes. The article was published in conference proceedings with no anonymous peer review.


A senior conservation scientist at the Canadian Conservation Institute performed an independent
evaluation of the PaperSaver deacidification spray developed by Joseph Zicherman of Provenance LLC. The spray contained alkaline oxides and carbonates. Acidic paper was sprayed and then artificially aged, and physical measurements were performed (tear resistance, folding endurance, zero-span tensile strength; ISO brightness, yellowness, and color; cold extraction pH; and alkaline reserve (AR)). Treatment had little effect on properties of unaged treated paper other than increasing the pH and providing an AR. However, aging stability was improved by a factor of ~ 3 over the controls even though treatment did not prevent decreases in tearing, folding, and breaking resistances. Treatment did not improve the ability of the paper to resist yellowing during aging. The article was published as a report with no anonymous peer review.


The Head of Paper Deacidification at the Swiss National Library discusses alkaline reserve (AR) in terms of neutralization chemistry and requirements for permanence. Using Papersave® Swiss, there was no relationship between paper pH and AR. Acidic groundwood paper that had an AR of at least 1.2% magnesium carbonate (equivalent to 1.4% calcium carbonate) retained an AR, remained alkaline, and had improved strength after artificial aging. Treatment, however, resulted in yellowing [alkaline darkening], but it retarded the more significant browning that occurred with untreated paper under artificial aging. The article was published in conference proceedings with no anonymous peer review.


The head of the Laboratory of the National Library of France describes results from a six-year study of four mass deacidification processes: Separex, Papersave® (Battelle), Bookkeeper®, and Sablé. At the time of the study, Neschen (Bückeburg) and Papersave® Swiss had not been developed. Separex was found to be unacceptable, with Papersave® (Battelle) and Bookkeeper® deemed best. However, the Papersave® (Battelle) process dissolved printing and writing inks, caused iridescence on illustrations, and deposited salts. Bookkeeper® deposited salts but did not harm illustrations or inks. Papersave® (Battelle) and Bookkeeper® gave comparable alkaline reserves and homogeneous distributions of magnesium Mg(II). The alkaline reserve (AR) for Bookkeeper® was in the form of tiny grains (1-2.5 microns (μm) in diameter) on the surface of the fibers. Papersave® (Battelle) did not deposit visible grains so the inference was that the AR was deposited not only on the fiber surfaces but also deep in their interiors. Neither process prevented loss of paper strength upon artificial aging, but the Papersave® (Battelle) process protected paper the best. Bookkeeper® was deemed the most appropriate, however, because it gave the least visible damage. The article was published in a newsletter with no anonymous peer review.


The head of the Laboratory of the National Library of France describes results from a research project to evaluate Bookkeeper®, Papersave® (Battelle), Neschen (Bückeburg), and Papersave® Swiss. Each process is described in detail. A useful table compares the processes in terms of active agent, solvent, surfactant, procedure, alkaline reserve agent, side effects, time required for the process, treatment capacity, and users, and is presented in multiple languages. All processes except for Neschen can treat books: Neschen only treats sheets of paper. The Papersave® processes needed pre- and post-treatment heat/vacuum drying of the objects; caused fading, inks to dissolve, iridescence on illustrations, and whitish deposits; and required one month of reconditioning. Bookkeeper® needed neither pretreatment nor reconditioning, but left a white deposit on book covers that had to be removed.
by wiping. Side effects from the Neschen process were not reported because they were the subject of an on-going study. The article was published in a newsletter with no anonymous peer review.


Researchers in the Department of Chemical Technology of Wood, Pulp and Paper of the Slovak University of Technology provide a list of patents from 1936-2004 for deacidification and strengthening of paper. The ideal deacidification process was described as: (1) effects of reagent must be permanent, (2) the reagents must be harmless for all book components, (3) the reagents must be safe for users, (4) the process must be applicable to all types of paper, (5) all acids in the paper must be permanently neutralized, (6) the pH of the deacidified paper should be between 7-8.5, (7) the alkaline reserve (AR) should be 2% calcium carbonate equivalent, (8) the distribution of pH and AR must be homogeneous, (9) the method should deacidify and strengthen the paper, (10) the method must not influence paper brightness, and (11) books and documents must not swell, deform, or otherwise change in appearance after treatment. The article was published in a journal with no anonymous peer review.


The vice-president of the Centre Interrégional de Conservation du Livre, co-owner of a patent for using aminoalkylalkoxysilanes for deacidification, discusses data presented in his series of articles on aminoalkylalkoxysilanes (Cheradame 2001, 2003, 2004, and 2005). A critical analysis by the author of this bibliography of all data presented to date indicates the following: Treated papers yellowed [most likely from Maillard (browning) reactions between the amino groups of the reagent and paper components (Kelly, 1979; Tanaka, 1993; Painter, 2001; Bosetto, 2002; De La Orden, 2002; Nursten, 2005; and Davidek, 2008)]; the treatments provided neither a reproducible level of alkalinity nor strengthening, particularly after artificial aging; there was no relationship between strengthening and neutralization of paper acidity; folding endurance (machine direction) of acidic paper decreased after treatment and aging; and the chemistry is neither "green chemistry", innocuous, nor inherently environmentally safe. The article was published in conference proceedings with no anonymous peer review.


The Director (Doffey) and Head of the Collection Department (Balzardi) of the Swiss National Library provide an introductory overview of the mass deacidification processes used in Europe and the US in 2006. A summary table is presented that describes the processes, the operating companies, where they are used, the chemical reagents, process procedure, treatment time, range of application, batch size, and main side effects. The article was published in conference proceedings with no anonymous peer review.

The Head of Historical Collections, Central and Regional Library Berlin, describes the logistics and other aspects of mass deacidification using the CSC Booksaver® process. The historical collections in need of deacidification included 19th and 20th century scholars' libraries. A major issue was mold, and mold spores were reported to settle preferentially on over-acidified paper facilitating their growth under relevant climatic conditions. Consequently, mold remediation (dry vacuum) was followed by mass deacidification. Books containing red stamps and leather bindings were studied. The CSC Booksaver® process did not cause bleeding of red stamping ink, and damage to leather bindings was negligible. However, fading of the print on individual pages did sometimes occur. Quality control standards including color change, visible deposits, structural changes to the surface of the paper, surface pH, distribution of magnesium carbonate, and degree of homogeneity were described. The article was published in conference proceedings with no anonymous peer review.


Scientists in the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan describe how sonication of paper dipped into an aqueous zinc oxide solutions destroys the paper quality. This is related to the Kundrot patent (Kundrot, 1999) that uses sonication of metal oxide particles in a gas-solid fluidized bed to deacidify papers and books. Sonication in a gas-solid fluidized bed may not degrade paper quality as does aqueous sonication, but the impact of sonication from a gas-solid fluidized bed on paper quality has not been reported. The article was published in a RSC (Royal Society of Chemistry) journal with anonymous peer review.


The Head of Conservation at the Swiss National Library (SNL) describes the selection criteria for mass deacidification of originals using the Papersave® Swiss process. The primary holdings of the SNL are from the time when paper mills primarily produced acidic paper (1870s and later). Monographs and other holdings, except for newspapers, that were selected for mass deacidification contained stronger paper and had been published after 1930. Quality standards are described for magnesium carbonate uptake, homogeneity of treatment, surface pH, color change, and visual-tactile changes. The article was published in conference proceedings with no anonymous peer review.


The Head of Preservation (Hanus) and others (Mináriková and Szabóová) from the Slovak National Archives; and others from the Department of Chemical and Food Technology, Slovak University of Technology (Katuščák and Čeppan); the Slovak National Library (Bukovský); the Polymer Institute, Slovak Academy of Science (Rychlý); and the University Library (Hanusová) describe the approach for preserving millions of archival and library materials that were produced on acidic paper from 1850-1900. The "KHIHA SK" research and development program is described, which included an evaluation of commercial mass deacidification processes by comparing pre- to post-treated materials in artificial
aging tests. A large number of physical and chemical parameters were tested, but no data are presented. The article was published in conference proceedings with no anonymous peer review.


The vice-president (Cheradame) and managing director (Ipert) of the Centre Interrégional de Conservation du Livre (Interregional Center for the Conservation of the Book), co-owners of a patent for using aminoalkylalkoxysilanes for deacidification, and researchers from CNRS (Dupont and Lavédrine), the CCI (Bégin), and the Laboratoire de Génie des Procédés Papetiers (Pulp and Paper Engineering Laboratory) (Rousset) studied the use of aminoalkylalkoxysilanes as paper strengthening reagents. Low-humidity artificial heat aging significantly decreased the folding endurance (FE) of papers treated with one silane, but after high-humidity artificial heat aging, the FE of treated paper was statistically the same as untreated paper (Table 4) [so no improvement occurred]. Conversely, treatment with another silane caused a significant decrease in FE, but FE of treated and untreated papers after high-humidity heat aging was statistically the same (Table 5) [so no improvement occurred]. The FE of paper treated with one silane decreased significantly after exposure to nitrogen dioxide (Table 4). A conclusion from size-exclusion chromatography (SEC) was that treatment prevented acid hydrolysis of cellulose, but this conclusion was not reconciled with either the decrease in FE after treatment or the failure of the treatment to stabilize paper under nitrogen dioxide and heat aging conditions. The article was published in an Elsevier journal with anonymous peer review.


Researchers in the Department of Applied Environmental Science, Stockholm University (Järnberg) and the Man-Technology-Environment research center at Örebro University (van Bavel) summarize the environmental levels and issues regarding perfluoroalkylated substances, which are relevant for evaluating the environmental impact of the perfluoropolyether acid surfactant used in the Bookkeeper® deacidification process. [The surfactant used in Bookkeeper® should be more biodegradable because of its ether linkages, and its biodegradation products should result in short-chain perfluorinated compounds that would not bioaccumulate and would not be biopersistent (Leiner and Kifer, 1993; Leiner et al., 1998; Leiner et al., 2000; Kissa, 2001; Zumbühl and Wuelfert, 2001; and Guo et al., 2008).] The article was published as a report with some peer review.


The Head of Training Programs, School of Conservation, The Royal Danish Academy of Fine Arts (Larsen) and researchers at the Royal Institute for Cultural Heritage Laboratory for Materials and Techniques, Belgium (Wouters); the CTBnF Laboratoire, France (Juchauld); and the Swiss National Library (Blüher) discuss the impact of Papersave® Swiss deacidification on leather bookbindings. Leather needs to remain slightly acidic to retain its tanning, but the Papersave® Swiss alkaline treatment solution dried and penetrated the leather. The treated leather became stiffer, darker, more yellow, and decreased in hydrothermal stability. Lubricants were extracted; tannin monomers increased; the opening angle of the front boards showed a significant decrease; and there was permanent damage with treatment and artificial aging. Consequently, the Swiss National Library postponed the use of the treatment for items with a high content of leather. The article was published in conference proceedings with no anonymous peer review.

The Head of Archives at the State Archive of the canton Basle Land, Switzerland, describes collection care that includes mass deacidification using the Papersave® Swiss process. Microfilm copies of the most valuable holdings were exclusively used for access; air conditioned storerooms and packing suitable for archives were used in repositories; and ~ 6-10 linear meters of documents were deacidified every two years using Papersave® Swiss. Newspapers (1830-1970), official publications (1833-2000), documents with mold damage (mainly from 19th century), and civil registers (1876-1959) were deacidified. The documents were bound in leather, cloth, or synthetic fibers, and contained different printing and stamping inks, none of which were damaged. The article was published in conference proceedings with no anonymous peer review.


A conservator at the Konservierung und Restaurierung von Schriftgut und Graphik, Switzerland, describes the history of the selection of the Papersave® Swiss process for mass deacidification of books. At the time, the three available processes were the FMC-Lithco MG 3 liquid process; the AKZO gaseous diethylzinc (DEZ) process; and the Battelle liquid process that used chlorofluorohydrocarbons (now called Papersave®). The two liquid processes provided for good penetration but caused inks and colors to bleed and left a deposit of magnesium salts. The DEZ process did not provide homogeneous deacidification, left Newton rings, and made synthetic binding materials sticky. Neither the FMC nor the DEZ processes became commercial successes. When chlorofluorohydrocarbons were banned, Battelle changed its solvent to hexamethyldisiloxane, a new active ingredient was introduced, and conventional pre-drying methods replaced microwave drying. The article was published in conference proceedings with no anonymous peer review.


Researchers from the Food Research Institute Bratislava (Polovka); the Institute of Polymer Materials (Polovka, Vizárová, Kirschnerová, Bieliková, and Vrška) and the Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology (Polovková) used Fourier transform spectroscopy (FTIR) to monitor the change of magnesium oxide to magnesium hydroxide and to address the rate of deacidification using Bookkeeper® deacidification reagent. Treated paper was artificially heat-aged at high relative humidities (81% and 98% RH). Transformation of magnesium oxide into magnesium hydroxide was exponentially dependent on temperature and RH. Detection of carbonyls decreased as detection of carboxylates increased with increasing time at high RH. This was interpreted to indicate neutralization and conversion of carboxylic acids into their carboxylate anions, which rate was RH-dependent. [Results at such high humidities may not entirely reflect natural aging under typical ambient conditions (Middleton et al., 1996). However, using Bookkeeper® under natural aging conditions results in formation of magnesium hydroxide that is converted into magnesium carbonates (Zumbühl and Wueffert, 2001).] The article was published in an Elsevier journal with anonymous peer review.

A conservation scientist at the National Library of the Netherlands gives a brief history of why the Bookkeeper® process was chosen for mass deacidification. In 1990, a damage survey showed that paper from the second half of the 19th and first half of the 20th centuries were most damaged. Available mass deacidification processes were Wei T'o®, Bookkeeper®, Battelle (Papersave®), and diethylzinc (DEZ). Bookkeeper® was chosen for its results, the technical design of the treaters, and because there was a Bookkeeper® plant in the Netherlands. The criteria used to select materials for deacidification included low surface pH as revealed by a pH pen, high lignin content as revealed by a phloroglucine spot test, and paper strength high enough to withstand movement of the sheets during treatment. The article was published in conference proceedings with no anonymous peer review.


Researchers in the Department of Chemistry at the University of Natural Resources and Applied Life Sciences (BOKU) (Austria) describe the use of fluorescent labels to determine oxidized groups in cellulose, which is a method to evaluate the impact of mass deacidification on long-term stability of paper. Approximately 5-20 mg of cellulosic material were needed. The final labeled cellulose was analyzed using either gel permeation chromatography (GPC) or visible microscopy. The technique was applied to evaluate the effect of corrosion and radiation on cellulose. The article was published in conference proceedings with no anonymous peer review.


The head of the company that provides Papersave® Swiss (Nitrochemie Wimmis AG, Switzerland) describes the history of the deacidification plant, which is the property of the Swiss Confederation but operated by Nitrochemie. Papersave® Swiss uses the "Battelle process," which is a non-aqueous solution of magnesium and titanium ethanlates ("METE 30") in hexamethyldisiloxane. Bound, unbound, and boxed collections were treated. Materials were first pre-dried for 48 h to < 1% moisture content by warming under vacuum; flooded with the deacidification solution for 2-3 h; post-dried for 24 h under vacuum; and then reconditioned for 3-4 weeks by air at a specified temperature and humidity being blown through the treated material. During treatment, the magnesium alcololate immediately neutralized available free acids, and during reconditioning, moisture and carbon dioxide converted excess magnesium alcololate into magnesium carbonate. The titanium ethanolate did not contribute to deacidification but was needed to solubilize the magnesium ethanolate, and it was converted into titanium dioxide during reconditioning. Logistical and quality control details are also discussed. The article was published in conference proceedings with no anonymous peer review.


Researchers in the Departamento de Conservação e Restauro (Sequeira) and the Departamento de Química (Cabrita), Universidade Nova de Lisboa, and the Instituto de Investigação Científica Tropical (Casanova), Portugal, compare effects of deacidification using a spray of nanoparticles of calcium
hydroxide dispersed in isopropanol to immersion in aqueous calcium hydroxide. Properties evaluated after artificial aging were pH, color, and degree of polymerization (DP) of plain papers and papers that contained iron gall ink. [The experiments were not performed at the same pH, and the concentration of calcium hydroxide in the spray for the different papers was not the same, so it is difficult to comparatively evaluate data derived from aqueous vs. nonaqueous, or plain vs. iron-gall inked papers. However, the data suggest that the aqueous calcium hydroxide treatments at pH 12 were superior to the non-aqueous treatments at pH 9 or 11 in terms of maintaining an alkaline pH and causing less darkening and yellowing after artificial aging. The aqueous treatment also seemed to be superior in terms of reducing depolymerization of both plain and iron-gall inked papers.] The article was published in an Elsevier journal with anonymous peer review.


The Head of Collection Care at the British Library reviews deacidification in relation to individual items and paper strengthening via graft copolymerization. There is not currently a mass deacidification program at the British Library. Individual items are outsourced or treated by in-house conservators using either aqueous magnesium bicarbonate or nonaqueous methylethylmagnesium carbonate in hexamethyldisiloxane. The INFOSAVE project (Rhys-Lewis, 2002a, 2002b; Rhys-Lewis and Walker, 2003) investigated the possibility of establishing a mass deacidification facility in the UK and included a "demonstrator project" in which seven commercial deacidification processes were compared. There were several disadvantages to the graft copolymerization method of paper strengthening. The final INFOSAVE report (Rhys-Lewis and Walker, 2003) gives the results from the comparative testing. The article was published in conference proceedings with no anonymous peer review.


The Head of the Preservation Department at the Landesarchiv Nordrhein-Westfalen Technisches Zentrum (Nordrhein-Westfalen Federal Archive Technical Center), Germany, describes the use of the aqueous Neschen (Bückeburg) process for mass deacidification. The purpose of the Neschen process is to deacidify and consolidate weak paper by using a single bath that contains the surfactants Rewin® and Mesitol® to fix writing and stamping inks, magnesium bicarbonate to deacidify, and methylcellulose to size/consolidate the paper fibers. Advantages were that decomposition products from cellulose and lignin were partially removed, and that the paper was strengthened by the methylcellulose. Disadvantages were that color changes could occur, stamping inks could bleed, color could transfer to the reverse side, stamp imprints could transfer to the conveyor belt and from there to succeeding papers, the paper was slightly cockled after drying and pressing, and the process was best used for single sheets because of technological considerations. The article was published in conference proceedings with no anonymous peer review.


A researcher at the Institute of Chemical Wood Technology, August Cieszkowski Agricultural University of Poznan, Poland, discusses how magnesium Mg(II) salts at alkaline pH of 11 is used to reduce the depolymerization of cellulose during hydrogen peroxide bleaching of pulp, which is relevant for understanding the impact of Mg(II)-containing deacidification reagents on the oxidative
depolymerization of cellulose in paper (Corbett, 1973; Sinky, 1973; Williams et al., 1977; Graves, 1981; Lienardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Baty and Sinnott, 2004; Logenius et al., 2008). When using hydrogen peroxide for industrial bleaching of pulp, transition metal ions, such as cobalt Co(II), iron Fe(III), copper Cu(II), and manganese Mn(II), first must be removed because they catalyze the decomposition of hydrogen peroxide to produce hydroxyl free radicals, which then oxidize and depolymerize cellulose. At alkaline pH, Mg(II) hydroxides complex with the transition metal ions and remove (precipitate) them from solution. Excess Mg(II) salts do not harm the cellulose in terms of depolymerization, but excess Mg(II) hydroxide does cause yellowing [alkaline darkening] that decreases the brightness of the pulp. [Alkaline darkening is also observed during high-temperature artificial aging of papers deacidified with alkaline Mg(II) compounds]. The article was published in a journal with anonymous peer review.

2005


Researchers at the National Institute of Standards and Technology (NIST) (Antonucci, Fowler, McDonough) and the American Dental Association Foundation (Dickens and Xu) discuss the chemistry of alkoxysilanes to form complex polymeric structures, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006, 2008). The polymerization chemistry gives rise to three-dimensional polymers called silsesquioxanes that have complex cyclic, cage-like, amorphous structures. A generalized structure showing the complexity is presented. The extent of reaction to give either dimers, trimers, tetramers, and ultimately silsesquioxanes is dependent on reaction conditions (pH, solvent, temperature, amount of water present). [Such polymers would be expected to irreversibly coat papers treated with aminoalkylalkoxysilanes (Didwania, 1968; Kelly, 1972; Tolgyesi and Bresak, 1977; Kelly, 1979; Adams and Giam, 1984; Johnson, 2001; Gelest, Inc., 2004; Lowell et al., 2004; Arkles 2006a and 2006b; Ebadi et al., 2009).] The article was published in a journal with no anonymous peer review.


A professor at the Staatliche Akademie der Bildenden Künste Stuttgart Studiengang Restaurierung und Konservierung von Graphik, Archiv- und Bibliotheksgut discusses criteria for selecting and using a mass deacidification process. Criteria included standards for treatment goals, selection criteria for collection materials, quality standards for the effectiveness of treatment, evaluation criteria for acceptable/unacceptable treatment side effects, guidelines for testing and documenting treatment, infrastructure within the institution to handle the collections, and a working relationship with the deacidification company. The selection process needed to address pros and cons of different treatment methods. Liquid processes were deemed possibly better than "dry" processes because they remove acidic degradation products, but they could cause bleeding of dyes and deformation, cockling, and blocking of paper. The dry methods could leave a powdery residue of calcium carbonate or magnesium oxide. Other criteria were also discussed, including the development of risk factors for different types of collection items (i.e., leather or parchment bindings, dyes, paper strength). Organization support was considered important because of the extensive amount of work needed in handling the collections before and after treatment. The article was published in a journal with no anonymous peer review.


The Director of the Art Conservation Research Center, Carnegie Mellon University (Whitmore) and co-
workers (Bogaard and Morris) studied the impact of "pH-neutral" salts on the deacidification of photooxidized Whatman filter paper (100% cellulose). [Calcium acetate was a selection even though it is not "pH-neutral" because it dissociates in water to produce the acetate anion (a weak base) that then reacts with water to produce hydroxide ions. This perhaps is why artificial heat aging resulted in an alkaline paper pH: Le Chatelier's Principle says that the weak base equilibrium would be driven toward products (hydroxide ions) as acetic acid was removed by volatilization.] The purity of the calcium chloride was not given, and even food grades contain calcium hydroxide, fluoride (a weak base), magnesium, iron, and other trace metals. It is not clear whether a statistical design was used, and data in graphs appear to only represent one data point. The methodology was not tested on other types of papers or papers that contained inks/media or binders. It was suggested that chloride ions could react with transition metals in paper during treatment so that the metals would be easy to wash away. [This is unlikely, however, because transition metal ions expected in paper do not react with chloride to make inert coordination complexes. The metal ions either are hydrated in dilute aqueous solution or would be more strongly coordinated to functional groups in the lignocellulose.] The article was published in an AIC (American Institute for Conservation) journal with anonymous peer review.


A researcher at the Slovak National Library describes experiments comparing the alkaline reserve (AR) measured by weighing papers before and after deacidification to AR determined by potentiometric titrations. The samples were extracted in water and directly titrated with hydrochloric acid (HCl). Although the original titration curves were not presented, pH data (Table 1) and the first derivative titration curves (Fig. 1) can be used to back-calculate the original curves. [The original titration curves for all the papers, except for a highly acidic paper that was not fully deacidified, appear simply to be curves that would be expected for a bicarbonate buffer system with pKa ~ 6. For a highly acidic paper in which there was no AR remaining after deacidification, the titration curve appears to simply be a curve expected for a weak acid with pKa ~ 5 (acetic acid pKa = 4.8). The titration data thus confirm the AR in the former case and the lack of AR in the latter case.] The standard method for determining AR, which is to add excess HCl to the sample and then back-titrate with sodium hydroxide (NaOH), was not used as a benchmark. Thus, it is not known whether these data provide the same value for the AR as would be obtained using the standard method. The article was published in a journal with no anonymous peer review.


This bulletin about pH indicators from Merck Chemical Co. introduces why using pH indicators to determine the pH of relatively anhydrous deacidified paper may not provide valid results. This is relevant for understanding why using the color change of Brilliant Yellow dye as a test of the deacidification efficacy of Bookkeeper® and other "dry" processes is not appropriate (Kidder et al.,1998). The "protein error" described is an analogy to what would occur when the pH-indicating dye absorbs onto paper. The dye would absorb so that the color-change inducing dissociative groups of the indicator would be "fixed" via hydrogen bonds to the lignocellulose. This would prevent their dissociation and consequent change color in response to the presence of a non-aqueous alkaline deacidification reagent until enough moisture was present to hydrate the dye (Taras, 1948; Timir-Balázsy and Eastop, 1998; Amelin and Tret'yakov, 2003; EMD Chemicals, Inc., 2005; Polymathic Analytical Labs, 2009). The article was published as a company bulletin.


Researchers in the Department of Chemistry and CSGI, University of Florence, Italy, (Giorgi, Dei, Gabbiani, Ninham, and Baglioni) and the Stazione Sperimentale, Carta Cartoni e Paste per Carta, SSCCP, Milan, Italy, (Bozzi) describe results from using nanoparticles of magnesium Mg(II) and calcium Ca(II) hydroxide to deacidify 18th century papers. Papers treated with either Mg(II) or Ca(II) hydroxide nanoparticles dispersed in 2-propanol were compared to papers treated with the Wei To®
deacidification reagent (methoxy magnesium methyl carbonate, MMC). The degree of polymerization (DP) and tensile strength were measured before and after artificial hydrothermal and photooxidative aging. It is not clear whether the molar amounts of the different deacidification reagents applied to the paper samples were identical, and the reproducibility of the experiments is not known. The data presented, however, suggest that all treatments negatively impacted the DP and tensile strength after treatment, with the Mg(II) and Ca(II) nanoparticles giving poorer results than Wei T'o®. In contrast, after artificial hydrothermal and photooxidative aging, the Mg(II) and/or Ca(II) nanoparticles may have given better results than Wei T'o® in terms of reducing paper decomposition. The article was published in an ACS (American Chemical Society) journal with anonymous peer review.


This is a short summary of the more detailed IPCC 2005 Special Report regarding the global warming potentials (GWPs) of ozone-depleting substances (ODSs) and their perfluorocarbon (PFC) and hydrofluorocarbon (HFC) substitutes, an issue relevant for mass deacidification processes that use either PFCs or HFCs as solvents (Bookkeeper® and CSC Booksaver®, respectively). This summary may be of use to policy makers and anyone who would like a brief introduction to the issue. More detail can be found in the Final Draft of the report (*IPCC Special Report, Final Draft, 2005*). The article was published as a report with extensive peer review.


This IPCC 2005 Special Report contains data for global warming potentials (GWPs) of greenhouse gases that can be used in conjunction with the EDGAR database (*EDGAR Fast Track 2000 Dataset, 2005*) to estimate GWPs of the perfluorocarbons (perfluoroheptane and perfluoroheptane, PFCs) in Bookkeeper®, and the hydrofluorocarbon (HFC) HFC-227ea (heptafluoropropane) in CSC Booksaver®, mass deacidification processes. HFCs and PFCs do not damage the ozone layer but have high GWPs because they have long atmospheric lifetimes and are highly absorptive in the infrared. The primary greenhouse gases CO₂, CH₄, and N₂O contribute to 99% of global warming. In contrast, all three fluorinated compounds emitted globally from all sources, which are primarily non-deacidification industries, contribute to less than 0.33% of global warming (less than 0.3% for HFC-227ea and less than 0.03% for perfluoroheptane plus perfluoroheptane). Regulations and cost restrict their release into the environment, so recycling is used. [Using data from the EDGAR database, the Library of Congress mass deacidification program using Bookkeeper® is estimated to contribute insignificantly to global warming (emissions of < 0.000026% of all global warming gases).] The article was published as a report with extensive peer review.


The vice-president (Cheradádame) and managing director (Ipert) of the Centre Interrégional de Conservation du Livre (Interregional Center for the Conservation of the Book), co-owners of a patent for using aminooalkylalkoxy silanes for deacidification, and a researcher from the Laboratoire de Génie des Procédés Papetiers (Pulp and Paper Engineering Laboratory) (Rousset) studied aminooalkylalkoxy silanes as deacidification and paper strengthening reagents. Using a 10% solution of one aminooalkylalkoxy silane as a strengthening polymer coating did not neutralize the starting acidity of "paper G" (see Table 8 in Cheradame, 2004) but increased its strength (Table 2, here). Artificial heat aging "paper F" treated with a 15% solution caused it to return to an acidic pH (Table 9 in Cheradame, 2004) but did not negatively impact paper strength (Tables 2 and 4, here). Breaking length (BL) was unrelated to folding endurance (FE) because treated "paper C" gave a 70% increase in BL but a 70%
decrease in FE (machine direction); and treated "paper K" (Cheradame, 2006) gave a 40% increase in BL, but a 60% decrease in FE. Treatment caused yellowing [probably from Maillard reactions (Kelly, 1979; Tanaka, 1993; Painter, 2001; Bosetto, 2002; De La Orden, 2002; Nursten, 2005; and Davidek, 2008)]. The article was published in a journal with no anonymous peer review.


Researchers in the School of Conservation at The Royal Danish Academy of Fine Arts (Larsen), the Laboratory for Materials and Techniques at the Royal Institute for Cultural Heritage, Belgium, (Wouters), the Centre de Recherches sur la Conservation des Documents Graphiques, France (Juchauld), and the Swiss National Library (Blüher) report the effects of the Papersave® Swiss mass deacidification treatment on vegetable-tanned historic and new bookbinding leathers. The treated leathers were also subjected to artificial aging (hydrothermal and pollutant gases). Treatment resulted in deacidification of acids in the historic leathers, an increase in hydrothermal stability of new leathers, but a decrease in hydrothermal stability of historic leathers. For all leathers, there was a negative impact on durability, fat compounds were extracted, and the leathers stiffened. The overall conclusion was that the leather part of bookbindings might be in danger of being affected negatively by the process. The article was published in conference proceedings with no anonymous peer review.


A librarian at the Royal Belgian Institute of Natural Sciences (RBINS) summarizes the mass deacidification program at the RBINS using CSC Booksaver®. Books were treated at the parent plant in Barcelona or at the Preservation Academy Leipzig (PAL). Books from 1840-1950 were selected, but books with a surface pH < 3 were considered too acidic and degenerated to support treatment. Negative side effects were observed for ~3% of the books, including stains, ink bleeding, ink movement, faded pictures, stuck sheets, white powdery residue, a very pronounced chemical odor, degreasing of leather bindings, and inhomogeneous treatment. Logistics, cost, and quality control parameters are also discussed. The article was published in a newsletter with no anonymous peer review.


In this monograph, a professor in the Department of Food Science and Technology, University of Reading, describes the chemistry of Maillard reactions, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). In particular, the lowering of pH (increasing the acidity) is one symptom of Maillard reactions because acetic acid is formed, the basic amino groups are converted into less basic heterocyclic compounds, and some nitrogenous compounds are lost as volatiles. [The amino groups of aminoalkylalkoxysilanes can be expected to undergo Maillard reactions with carbohydrates and other components of paper, which would be expected to increase the acidity of the paper over time (Kelly, 1979; Tanaka, 1993; Painter, 2001; Bosetto, 2002; De La Orden, 2002; and Davidek, 2008).]


The Emission Database for Global Atmospheric Research (EDGAR) information system, a joint project of the Netherlands Environmental Assessment Agency (PBL) and the Joint Research Centre, Institute for Environment and Sustainability (JRC-IES) of Italy, stores global emission inventories of greenhouse gases that are relevant for evaluating the global warming potentials (GWPs) of solvents used in Bookkeeper® (perfluorohexane and perfluoroheptane, both perfluorocarbons, or PFCs) and CSC
Booksaver® (heptafluoropropane, HFC-227ea, that is a hydrofluorocarbons, or HFC) deacidification processes. EDGAR in conjunction with GWPs from the IPCC Special Report, Final Draft (2005) can be used to estimate GWPs of the primary greenhouse gases, CO₂, CH₄, and N₂O that contribute to 99% of global warming, and the non-ozone-depleting but long-lived and highly infrared absorptive HFCs and PFCs. All three fluorinated compounds emitted globally from all industries, which are primarily non-deacidification industries, contribute to less than 0.33% of global warming (less than 0.3% for HFC-227ea and less than 0.03% for perfluorohexane plus perfluoroheptane). Regulations and cost restrict their release into the environment, so recycling is used. [Using data from the EDGAR database, the Library of Congress mass deacidification program using Bookkeeper® is estimated to contribute insignificantly to global warming (emissions of < 0.000026% of all global warming gases).] The database was published with extensive peer review.

2004


Researchers from the Laboratory for Physicochemical Analysis and Structural Research and the Department of Chemistry, Jagiellonian University, Krakow, Poland, present an overview of paper acidity and acid-catalyzed degradation of paper. The source of acidity in alum-containing paper is the hydrated aluminum Al(III) ion, which is comparable to acetic acid in acid strength (pKa ~ 5). The mechanism for acid-catalyzed hydrolysis involves cleavages of glycosidic bonds between the glucose units in cellulose, which would be a random process if all glucose units were identical. However, cleavages of some glycosidic bonds are more favorable because of the presence of carbonyl or other functional groups in the glucose ring. The Zou, Ueska, and Gurnagul kinetic model is described, in which the pre-exponential factor in the Arrhenius equation is dependent on the initial acidity of the paper and its moisture content. Arrhenius plots indicate that cellulose hydrolysis has an activation energy (Eₐ) of ~ 104-113 kJ mol⁻¹. Cellulose oxidation, which is more prevalent at higher temperatures, has an Eₐ of ~ 70-80 kJ mol⁻¹ and results in formation of carboxylic acids. Higher temperatures with constant Al(III) content caused the pH of acidic paper to become even more acidic and increased the impact of oxidation. The article was published in a book with no anonymous peer review.


Researchers in the Department of Textiles and Paper, UMIST (Baty) and the School of Applied Sciences, University of Huddersfield (Sinnott) describe the aqueous hydrolysis of 1,5-anhydrocellobiitol (a model for cellulose) in the presence of aluminum Al(III) ions at highly acidic pH. This research is relevant for understanding the chemistry involved in degradation of acidic paper that contains alum-rosin sizing. Increasing concentrations of Al(III) resulted in an increase in the rate of acid hydrolysis at constant pH values of 3.0-3.3. Increasing concentrations of lanthanum La(III) ions, the control, had virtually no impact. At acidic pH, Al(III) might be a Lewis acid catalyst for acid hydrolysis. [However, for deacidified paper at alkaline pH, Al(III) and similar Lewis acids including magnesium Mg(II) ions would be complexed as insoluble hydroxides and/or carbonates, which would preclude their reactions as Lewis acid catalysts (Corbett, 1973; Sinky, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavrilii et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). The implication of the results is that acidic alum-rosin sized and any other paper that contains Lewis acid metal ions need to be a particular focus of deacidification.] The article was published in a RSC (Royal Society of Chemistry) journal with anonymous peer review.

Scientists at Miami University, Miami, FL (Coffin) and STFI-Packforsk, Stockholm, Sweden (Lif and Fellers) provide insight into the molecular features of paper that influence tensile strength (TS), which is relevant for understanding evaluations of the impact of deacidification on paper strength (Williams and Krasow, 1973; Williams et al., 1977; Tang and Jones, 1979; Caulfield and Gunderson, 1988; Daniels, 1989; Nissan and G. L. Batten, 1990; Padanyi, 1993; Brandis, 1994; Harris, 1995; Havermans et al., 1995; Moropoulou and Zervos, 2003; Karademir et al., 2004; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006). Measurements of TS, the amount of force (stress) needed to stretch (elongate) paper to its breaking point, are sensitive to the strain rate and the moisture content of the paper, and differ in the machine direction (MD) vs. cross direction (CD). Faster strain rates result in higher values of TS because of the slow viscoelastic relaxation behavior of paper. At slow rates of elongation, the cellulose fibers have more time to relax, so that increasing force results in a proportionately greater amount of stretch, thus reducing TS. Cellulose fibrils are comprised of crystalline regions unaffected by moisture, and amorphous regions that absorb water and become plasticized. As the majority of cellulose fibers are aligned in the MD, the MD tensile strength is primarily controlled by the axial stiffness of the crystalline regions. In the transverse direction, fiber stiffness is primarily controlled by the stretchier amorphous regions so that increasing moisture content decreases the TS in the CD more significantly. The article was published in a journal with anonymous peer review.


This product brochure from Gelest, Inc., lists the specific wetting surfaces (SWS) of aminoalkylsilanes, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). The SWS of 3-aminopropyltriethoxysilane in conjunction with data for internal surface area of papers given in Didwania (1968) can be used to calculate the amount of the silane needed to obtain a minimum uniform multilayer coverage on typical papers. The results can be used to better evaluate the physical meaning of the pseudo-adsorption isotherm shown in Cheradame (2004).


This Request for Proposals from 1990, drafted by the Preservation Projects Director of the Library of Congress, contains the original technical requirements for the Library of Congress mass deacidification program. Included are logistical, quality assurance, chemical, toxicological, and environmental impact requirements. The offeror was required to disclose the process chemistry and the chemical identity, physical form, concentration, and quantity of all chemical reactants and components retained in treated books; demonstrate the efficacy of the process including alkaline reserve and folding endurance data after artificial hydrothermal aging of acidic, newsprint, coated, highly filled, highly calendared, strong, weak, sized, and optical whitener-containing papers. The offeror was also required to show that the pH of treated paper ranged from 6.8-10.4; the alkaline reserve was uniform and at a minimum level of 1.5% calcium carbonate equivalent; the brightness after aging was at least as bright as an untreated control; the process did not extract any colored materials from inks, bindings, or colored illustrations; no odor remained after treatment; and the degree of photosensitivity of paper was not negatively impacted by treatment (determined by folding endurance after artificial humid light aging). Other requirements are described in detail. The article was published as a report with no anonymous peer review.


Researchers at TNO Buildings and Construction Research, Delft, The Netherlands (Havermans) and the Bibliotheque Nationale de France (Buisson) provide a summary of a project to test four mass deacidification processes. Several acidic reference papers were specifically manufactured for the...
Sablé and Papersave® (Battelle) resulted in residual odors from the treatment chemicals; Bookkeeper® gave no odor. The impact of treatment on folding endurance depended on the type of paper treated. For bleached sulphite softwood and acidic mechanical pulp papers, folding endurance decreased significantly after deacidification. However, for pre-aged acidic sulphite softwood paper, folding endurance increased slightly after treatment with Bookkeeper®. For all treatments, edges of the books received a higher level of alkalinity than the gutter. Papersave® (Battelle) and Bookkeeper® gave a comparable alkaline reserve (AR) and protection from airborne acidity, but the amount of AR depended on paper porosity. The article was published in conference proceedings with no anonymous peer review.


Researchers at Preservation Academy Leipzig (PAL) (Henniges), the Staatliche Akademie der Bildenden Künste Stuttgart (Banik), and the Christian-Doppler-Institut für Zellstoffreaktivität (Potthast) briefly describe results from using CSC Booksaver® spray on copper Cu(II)-corroded paper and archival material. Copper acetate was printed onto gelatin-sized rag papers, and the papers were heated and humidified to initiate copper corrosion. The papers were then either sprayed with CSC Booksaver® containing 15% of the deacidification reagent in 1-propanol or immersed into an aqueous solution of magnesium bicarbonate. After artificial aging and analyses of the results, the conclusion was that magnesium compounds were only able to reduce the oxidative action of Cu(II) if they were applied by non-aqueous means. [This conclusion is opposite to that of Shahani (1995) who showed that immersion into aqueous solutions of bicarbonates extracted Cu(II) from the paper, which consequently reduced degradation, but spraying aqueous and non-aqueous solutions had no effect because no extraction of Cu(II) occurred.] The bleeding of inks and dyes that occurred during immersion in Booksaver® was avoided by using the spray because it was directly controllable by the user. The article was published in conference proceedings with no anonymous peer review.


Scientists at the KSU (Karademir and Çetin) and Kafkas University (İmamoğlu) Departments of Forest Ind. Eng., Turkey, describe results from mechanically testing several papers, which is relevant for understanding tearing resistance, folding endurance, and tensile strength of paper before and after deacidification (Williams and Krasow, 1973; Williams et al., 1977; Coffin et al., 2004; Tang and Jones, 1979; Caulfield and Gunderson, 1988; Daniels, 1989; Nissan and G. L. Batten, 1990; Padanyi, 1993; Brandis, 1994; Harris, 1995; Havermans et al., 1995; Moropoulou and Zervos, 2003; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006). Interfiber bonding, an importance factor in paper strength, is determined by the fiber conformability, flexibility, collapsibility, and total surface area. Bleached fibers have higher bonding strength than unbleached fibers. Low lignin, low xylan, and high hemicelluloses on the fiber surfaces improve bonding strength. Beating causes external fibrillation of the fibers, creating new surfaces that can bond. Kraft softwood, refiner mechanical, and cotton linter pulps were formed into handsheets and tested. The kraft paper was the densest, had the highest tear index, folding endurance, tensile strength, tensile energy absorption (TEA), tensile index, and Young's modulus (stiffest of the papers). The refiner mechanical pulp paper was less dense than the kraft paper, but had the same density as the cotton paper. Its tear index, folding endurance, tensile strength, TEA, tensile index, and Young's modulus were all more than that of the cotton paper. The cotton paper fibers did not contain internal or external fibrillations, and had poor interfiber bonding that lead to its weaker strength. The article was published in a journal with anonymous peer review.

Researchers at the National and University Library of Slovenia (Kolar and Malešič), the University of Ljubljana, Slovenia (Strlič), and the Centre National d'Evaluation de Photoprotection Ensemble Universitaires des Cézeaux, France (Lemaire and Fromageot) describe the effect of light on the degradation of deacidified paper. Most of the damage to cellulose exposed to sunlight occurred at wavelengths of 300-500 nm, which was not a result of direct photolysis of cellulose but the result of decomposition of hydroperoxides and/or ketone groups in the cellulose that produced reactive agents that oxidized the cellulose. The use of viscometry to determine the degree of polymerization of irradiated cellulose was preferred over size exclusion chromatography (SEC) because SEC was deemed time-consuming, the data less reproducible, and having systematic errors difficult to evaluate. When 100% cellulose paper was deacidified, it degraded at a higher rate from photooxidation if it had been treated with magnesium Mg(II) carbonate at pH 9.35 than with calcium Ca(II) carbonate at pH 8.35. [The significantly higher pH of the Mg(II)-treated papers may account for the increased oxidation, but this important variable was not discussed.] The article was published in a book with no anonymous peer review.


In this monograph, researchers at Quantachrome Instruments (Lowell, Thomas, and Thommes) and Long Island University (Shields) describe the derivation of the Langmuir and BET adsorption isotherms and how to obtain them from gas-phase adsorption measurements, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). A pseudo-adsorption isotherm is shown in Cheradame 2004, the physical meaning of which can be better elucidated by understanding adsorption isotherms.


Researchers at the School of Chemical Science, University of Illinois at Urbana-Champaign (Prozorov and Suslick) and the Department of Physics & Astronomy, University of South Carolina (Prozorov) describe the high particle velocities that approach 170 m s⁻¹ (half the speed of sound) when solids are sonicated in liquids, which is related to the Kundrot patent (Kundrot, 1999) that uses sonication of metal oxide particles in a gas-solid fluidized bed to deacidify papers and books. In liquid sonication, the impact between metal particles can result in their melting (Prozorov et al., 2004; Colvin, 1976; Kolpak, F. J. and J. Blackwell, 1975). Sonication in a gas-solid fluidized bed may not harm paper as might aqueous sonication, but the impact of sonication from a gas-solid fluidized bed on paper has not been reported. The article was published in an ACS (American Chemical Society) journal with anonymous peer review.


The vice-president (Cheradádame) and managing director (Ipert) of the Centre Interrégional de Conservation du Livre (Interregional Center for the Conservation of the Book), co-owners of a patent for using aminoalkylalkoxysilanes for deacidification, and a researcher from the Laboratoire de Génie des Procédés Papetiers (Pulp and Paper Engineering Laboratory) (Rousset) studied aminoalkylalkoxysilanes as liquid-phase deacidification reagents (Didwania, 1968; Kelly, 1972; Tolgyesi and Bresak, 1977; Kelly, 1979; Adams and Giam, 1984; Johnson, 2001; Gelest, Inc., 2004; Lowell et al., 2004; Antonucci et al., 2005; Arkles 2006a and 2006b; Ebadi et al., 2009; Gelest, Inc., 2009). Papers treated with either 9% or 15% solutions had initial alkaline surface pHs, but the pH and alkalinity decreased significantly after artificial heat aging (Tables 7 and 9). Papers treated with 10% solutions followed by natural aging for eight months either did not provide or barely provided enough alkalinity to neutralize the initial paper acidity (Table 8). Papers treated with 15% solutions (Table 8) acquired
enough alkalinity to neutralize the initial paper acidity so that a true reserve of alkalinity remained on the paper (2.4% CaCO₃ equivalent). However, after natural aging for four months, there was a decrease in surface pH by one pH unit although the alkalinity was approximately the same (Table 8). The article was published in a journal with no anonymous peer review.


A preservation specialist at the Library of Congress provides an overview with many photographs of the mass deacidification program at the Library of Congress (in Spanish). The Library started using the Bookkeeper process in 1996, and obtained approval from the US Congress for a 35-year program, to mass deacidify books, comics, manuscripts, and other materials that contain acidic paper. Items that contain materials susceptible to pH-dependent color change cannot be treated, but some photographs are amenable to the process. [The source of paper acidity, however, is not from alum forming sulfuric acid (pKa of -3) upon reaction with water in paper, as is stated. When alum is added to water at the wet-end of the papermaking process, it forms hydrated aluminum Al(III) ions that then undergo hydrolysis. The pKa of the hydrolysis reaction is 4.7, comparable to the pKa of acetic acid (4.8), so that the hydrated Al(III) ion is a weak, not a strong, acid.] A large wave of conversion to alkaline papermaking was begun in the 1980s by many industrial manufacturers of paper in Europe and the US because of the superior quality of the paper at a lower cost. The article was published in a magazine with no anonymous peer review.


Researchers at the University of Ljubljana, Slovenia (Strlič and Kočar), the National and University Library of Slovenia (Kolar), and the Polymer Institute of the Slovak Academy of Sciences (Rychlý) describe oxidative and alkaline degradation of paper, pathways for degradation of deacidified paper at alkaline pH. Deacidified bleached chemical pulps have higher levels of carbonyl groups from the bleaching process and were more prone to autooxidation and yellowing [alkaline darkening] during artificial heat aging. Increasing relative humidity (RH) during heat aging increased the degradation of acidic paper but had no statistically significant effect on the degradation of alkaline paper. Experimental uncertainty makes it difficult to assess the impact of RH on degradation of papers deacidified with calcium Ca(II) and magnesium Mg(II) carbonates, but their degradation was significantly less than that of acidic papers at higher RH. A lower activation energy (Eₐ) was reported for degradation of bleached pulp under dry conditions (93 kJ mol⁻¹) compared to humid conditions (126 kJ mol⁻¹), and heat aging of Ca(II) and Mg(II) treated cellulose papers at 65% RH gave activation energies of 99-102 kJ mol⁻¹ for depolymerization with Mg(II) causing slightly less degradation than Ca(II) (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavrilii et al., 2001; Malesić et al., 2001; Mordasini et al., 2003; Strlič et al., 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). Mg(II) treated papers yellowed more [perhaps because of their higher pH.] The article was published in a book with no anonymous peer review.


Researchers at the University of Ljubljana (Strlič, Kočar, Šelihi, Susić, and Pihlar), the National and University Library, Slovenia (Kolar), and the Pulp and Paper Institute, Slovenia (Kočar) compared seven methods for measuring the pH of paper. Using pH electrodes and cold extraction gave readings for alkaline papers that changed with equilibration time with atmospheric carbon dioxide. Surface measurements gave systematically low (more acidic) values, particularly for alkaline papers; pH pens and a micro-pH electrode gave systematically low values by as much as 2-4 pH units, particularly for gelatin surface-sized papers. Colors of pH indicators for alkaline papers were dependent on humidity (Taras, 1948; Tímír-Balázs and Eastop, 1998; Kidder et al., 1998; Amelin and Tretyakov, 2003; EMD
Useful data for understanding the chemistry of carbonates and bicarbonates was presented, and the discussion of problems with measurements of paper pH is excellent. [In essence, measurements of pH of alkaline paper are fraught with error, and different methods can be expected to give different results, as also shown by Kelly (1972). Kelly (1972) also showed that pH measurements do not always reflect the true acidity or alkalinity of paper, and that hot extraction was significantly better than cold extraction for measuring paper pH.] The article was published in a journal with no anonymous peer review.


Researchers at the University of Ljubljana, Slovenia (Strlič, Kočar, Šelih, and Pihlar), the National and University Library of Slovenia (Kolar and Malešič), the Polymer Institute of the Slovak Academy of Sciences (Rychlá and Rychlý), the Netherlands Institute for Cultural Heritage (Haillant, Pedersoli, and Scholten), and the Centre National d'Evaluation de Photoprotection Ensemble Universitaire des Cézeaux, France (Fromageot and Lemaire), discuss results from deacidification using aqueous magnesium Mg(II) and calcium Ca(II) carbonates. For Whatman 100% cellulose paper, maximizing the alkaline reserve with Mg(II) carbonate gave a pH ~ 10, whereas Ca(II) carbonate gave a pH ~ 8.5. For rosin-sized papers, both carbonates give a pH ~ 9. The activation energy (E_a) for thermooxidation at 65% relative humidity of high cellulose papers deacidified using either carbonates was ~ 100 kJ mol⁻¹. Papers deacidified and then treated with antioxidants yellowed more than untreated papers. For an acidic high cellulose paper, Mg(II) carbonate deacidification gave a stabilization factor twice as great as Ca(II) carbonate. For a significantly older ground wood paper, Mg(II) carbonate gave a stabilization factor 21 times greater than Ca(II) carbonate (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malešic et al., 2001; Mordasinii et al., 2003; Strlič et al., 2004a, 2004c; Baty and Sinnott, 2004; Wójciak, 2006; Lumenius et al., 2008). Results from using unsized Whatman paper did not particularly reflect results from real-life paper samples. The article was published in a book with no anonymous peer review.


Researchers at the University of Ljubljana, Slovenia (Strlič and Kočar), the Polymer Institute of the Slovak Academy of Sciences (Rychlá), the Netherlands Institute for Cultural Heritage (Haillant), and the National and University Library of Slovenia (Kolar) describe the use of chemiluminescence to evaluate the oxidative degradation of paper, which is an important reaction for degradation of deacidified paper at alkaline pH and high temperature. In artificial aging experiments at temperatures > 100 °C, the activation energy (E_a) for thermooxidative depolymerization of paper determined from viscosity measurements was 101 kJ mol⁻¹, similar to values reported by other researchers. This contrasts with the 54-60 kJ mol⁻¹ E_a determined from chemiluminescence measurements, which indicates that the chemiluminescent signal was caused by other more facile and faster reactions in addition to cellulose thermooxidation. [This suggests that chemiluminescence is not a specific enough analytical technique to use to quantitatively measure the oxidation of paper.] The presence of magnesium Mg(II) carbonate significantly increased the stability of cellulose at artificial aging temperatures < 200 °C (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malešic et al., 2001; Mordasinii et al., 2003; Strlič et al., 2004a, 2004c; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). The article was published in a book with no anonymous peer review.

A conservator at the Koninklijke Bibliotheek, The Hague, Netherlands, reviews a number of research areas regarding paper degradation and treatments, including mass deacidification. Brief summaries are provided regarding institutions that were using Wei T'o®, Neschen (Bückeburg), Papersave® (Battelle), and Bookkeeper®. General conclusions about the mass deacidification processes of 2004 were that managers should not hope to deacidify a whole collection in a single mighty effort, and that some methods were not amenable to leather, plastics, inks, dyestuffs. However, after artificial aging, the quality of an acidic paper that had been mass deacidified was better than if it had not been treated, including yellowing. The article was published in a book with no anonymous peer review.

2003


Researchers in the Department of Chemistry and Ecology, Vladimir State University, Russia describe the absorption of azo dyes to cellulose (paper). This is relevant for understanding why using the color change of Brilliant Yellow dye as a test of the deacidification efficacy of the Bookkeeper® process is not a valid indicator of pH (Kidder et al., 1998). Brilliant Yellow pH indicator has a high affinity for cellulose. Absorption of the dye onto paper results in a shift of its absorption band, which indicates that the phenolic color-change inducing groups of the dye are hydrogen bonded to the paper. [The phenolic groups, whose ionization/dissociation in water results in a color change from yellow (acidic) to orange (basic), will not ionize/dissociate and cause a color change if absorbed on paper in the presence of a non-aqueous deacidification reagent unless sufficient moisture is present so that the dye can be solvated and the hydrogen bonds broken. This is why Brilliant Yellow and similar dyes absorbed onto paper prior to a non-aqueous deacidification treatment would not be expected to change color to indicate the extent of deacidification until the paper was exposed to high humidity (Taras, 1948; Tímír-Balázsy and Eastop, 1998; Kidder et al., 1998; Strlič et al., 2004b; EMD Chemicals, Inc., 2005; Polymathic Analytical Labs, 2009).] The article was published in a Springer journal with anonymous peer review.


Researchers in Chemistry at Jagiellonian University (Barański, Łojewski) and the Jagiellonian Library (Frankowicz, Harnicki, and Koziński), Craków, Poland, describe results from testing with a pH pen the acidity of over 11 thousand books from the years 1938-2001 randomly selected from the > million book collection at the Jagiellonian Library. From the years 1939-1985, almost 100% of the books were printed on acidic paper. This dropped to ~ 90% by 1995, to ~ 3.5% in 1998, and to ~ 0.7% in 2001. The results were comparable to those from other Polish libraries. They suggest that performing a similar experiment at a large national library in another country might provide an estimate of the number of acidic books in any other library in the country. The article was published in conference proceedings with no anonymous peer review.


The vice-president (Cheradádame) and managing director (Ipert) of the Centre Interrégional de Conservation du Livre (Interrregional Center for the Conservation of the Book), co-owners of a patent for using aminoalkylalkoxysilanes for deacidification, and a researcher from the Laboratoire de Génie des Procédés Papetiers (Pulp and Paper Engineering Laboratory) (Rousset) studied vapor-phase reactions between acidic papers and silazanes, trimethylsilylimidazole, and aminoalkylalkoxysilanes. The first premise was that the silazanes and imidazoles would react with active hydrogens in the paper via silanization reactions to liberate amines to neutralize the acidity. After vapor-phase treatment and then ambient storage, the surface pH of the papers either decreased to below 7.5 (the lowest acceptable value) or if they increased to above 7.5, non-volatile amines were formed that would remain on the...
paper and pose a health hazard. A second premise was that aminoalkylalkoxysilanes would react with ambient moisture to undergo hydrolysis and self-polymerization reactions to produce polymeric coatings whose free amino groups would neutralize the acidity (Didwania, 1968; Kelly, 1972; Tolgyesi and Bresak, 1977; Kelly, 1979; Adams and Giam, 1984; Johnson, 2001; Gelest, Inc., 2004; Lowell et al., 2004; Antonucci et al., 2005; Arkles 2006a and 2006b; Ebadi et al., 2009; Gelest, Inc., 2009). However, after vapor-phase reaction and ambient (natural) storage, the surface pH of the papers was below 7.5. All results were judged unsatisfactory. The article was published in a journal with no anonymous peer review.


Researchers from TNO Building and Constructions, Delft (Havermans), Shell Research & Technology Center, Amsterdam (Genuit), and TNO Industrial Technology, Enschede (Penders), The Netherlands; and the French National Library, Paris, France (Buisson) describe results from testing paper after it was deacidified using the Separex, Sablé, Papersave® (Battelle), and Bookkeeper® mass deacidification processes and stored for six months in a well-ventilated room at ambient temperature and humidity. Parameters tested included acidity (pH), alkaline reserve (AR), and volatile organic compounds. All processes except Separex neutralized the paper acidity and provided an AR. Papers treated using the Sablé and Papersave® (Battelle) processes emitted a number of alcohols in relatively high concentrations, and well-ventilated storage was recommended. The Papersave® (Battelle) process also resulted in the emission of organo silane compounds and dimethylsilanol. Bookkeeper® resulted in the emission of trace levels of perfluorinated hydrocarbons. The article was published in conference proceedings with no anonymous peer review.


Researchers in the Textile Engineering Department, Amir Kabir University of Technology, Iran, provide a succinct and well-presented description of methodology and results from studying the degradation of cotton (cellulose) fibers. They provide descriptions of and results from eight simple analytical methods that may be used to test the impact of artificial and natural aging on paper (cellulose). These include tests to determine the degree of polymerization (DP) using viscometry; carboxyls using the methylene blue test and the sodium bicarbonate-sodium chloride solution test; carbonyls using the 2,4-dinitrophenyl hydrazine test; aldehydes using Fehling's solution; surface modifications by the vertical wicking test and Fourier transform infrared spectroscopy (FTIR); and yellowing by colorimetry. The methylene blue test was not a good method for measuring carboxyls because of changes in the scattering coefficient of the cellulose fibers because of degradation. The article was published in a journal with anonymous peer review.


Researchers from IBM Research, Zurich Research Laboratory, Switzerland, describe results from computational modeling that reveal why magnesium Mg(II) reacts significantly differently from Ca(II) in enzymatic systems, which is relevant for understanding the effects of Ca(II) and Mg(II) salts as deacidification reagents and on the oxidation of paper (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malešić et al., 2001; Strlič et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójcik, 2006; Logenius et al., 2008). A combined quantum mechanical and molecular mechanics model reveals that it is not the greater relative Lewis acidity of Mg(II) vs. Ca(II) that causes Mg(II) to be a cocatalyst while Ca(II) is instead an enzymatic reaction inhibitor. It is instead that Mg(II) reduces the transition state energy of the enzymatic reaction because Mg(II) can stabilize a
pentacoordinate transition state by being able to reduce its coordination with oxygen from six to four, which is not uncommon for Mg(II). In contrast, Ca(II) tends to "over coordinate" in reference to six-fold coordination so that it always maintains six-fold coordination, which increases the energy of the reaction transition state. [This type of coordination-driven chemistry might account for some differences in how Mg(II) and Ca(II) interact with cellulose and other components of paper, and why they impact oxidative degradation rates differently.] The article was published in a journal with anonymous peer review.


Researchers in the Department of Library Science and Information Systems, Technical Educational Institution of Athens, Greece, describe the impact of soaking paper in two deionized water baths followed by another bath of either deionized water, a "semi-saturated" calcium hydroxide solution (pH 12.1-12.2), and/or a 1% methylcellulose solution in deionized water, which is relevant for understanding the impact of aqueous mass deacidification processes, such as the Neschen (Bückeburg) process, on paper. The dry tensile strength (TS) of papers decreased after soaking in deionized water and deacidification, but increased after soaking in deionized water followed by deacidification and treatment with methylcellulose. The conclusion was that interfiber bonding was negatively affected by immersion in water and subsequent drying. [These results are not surprising because they mirror data and conclusions first published 30 years ago (Tang and Jones, 1979; Tang, 1981; Nelson et al., 1982). The deleterious effect on TS of soaking/washing paper in deionized water is why conservators, as per the advice in the Paper Conservation Catalog, 7th Edition, 1990, http://cool.conservation-us.org/coolaic/sq/bpg/pcc/16_washing.pdf, avoid washing paper in deionized water. It would have been useful to compare the folding endurance (FE) of the papers to their TS, because washing is expected to increase the FE while decreasing the TS (Williams and Krasow, 1973; Williams et al., 1977; Coffin et al., 2004; Tang and Jones, 1979; Caulfield and Gunderson, 1988; Daniels, 1989; Nissan and G. L. Batten, 1990; Padanyi, 1993; Brandis, 1994; Harris, 1995; Havermans et al., 1995; Karademir et al., 2004; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006;)] The article was published in a journal with no anonymous peer review.


The Head of Preservation, Yale University Libraries, discusses selection criteria and other workflow issues when selecting mass deacidification as a preservation option. A major factor that influenced the selection of mass deacidification was that it preserved the original object, which is a format that some research studies required. Microfilming and digitizing only saved the intellectual content. Microfilming was relatively expensive and the negatives had to be maintained as well as the viewing machines. Digitizing was less expensive in terms of image capture, but there were cataloging costs associated with creating metadata; the digital files had to be maintained; and digital files had to be prepared that would be accessible either via the web, a workstation, DVD, or CD. Collection selection criteria for mass deacidification included that the pH of the text block was less than 7 by chlorophenol red pH pen, the paper was neither glossy nor contained a coating, the paper was flexible, and the text block was sound (no splits, tears, or loose pages). The article was published in conference proceedings with no anonymous peer review.


A consultant in preservation and collections management (Rhys-Lewis) and the Head of Programmes at the National Preservation Office, UK (Walker) describe the INFOSAVE project comparing several mass deacidification processes (Rhys-Lewis, 2002a, 2002b). A useful summary table is provided.
Bookkeeper® gave consistent alkaline results, a slight slick feel from powdery deposits; CSC Booksaver® gave inconsistent results, tidemarks, white deposits, ink bleed, and odor; Libertec® gave some variation in results, patchy white deposits throughout the text block, and required extensive protective packaging; Neschen (Bückeburg) was unable to process books, archive material showed cockling, and there was some ink run; Papersave® Swiss gave consistent results, no physical effects, there was color bleed from red binding material, slight yellowing on edges of illustrative plates, some odor in archive material, and required extensive protective packaging; and Papersave® (ZFB) gave consistent results, no physical effects, red binding material was not treated because of risk of ink run, alkaline material was not treated, and there was a strong odor. The Appendices give useful details regarding the processes, project specifications, selected collection materials, details from before-and-after visual and haptic analyses, and results of analytical tests. The article was published as a report with external validation and review.


A scientist at the University of Ljubljana (Strlič) and the head of the Conservation Department of the National and University Library (Kolar), Ljubljana, Slovenia, review research in paper stability including mass deacidification. Factors that influence paper stability include endogenous factors (pH, metal ions, lignin, and degradation products) and exogenous factors (temperature, humidity, oxygen, light, pollution, dust, microbes). A successful mass deacidification process was described as one that neutralizes paper acidity, leaves a uniform and sufficient alkaline reserve, should not harm any library material, and should not change paper appearance or physical properties. The article was published in conference proceedings with no anonymous peer review.

2002


Researchers at the Dipartimento di Scienza del Suolo e Nutrizione della Pianta, Universitàdi Firenze (Bosetto and Arfaioli) and the Istituto per la Genesi e l’Ecologia del Suolo (IGES) CNR, Firenze (Pantani) studied the Maillard reaction between glycine and glucose in the presence of cations and clays, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). A noted drop in pH occurred after 30 days, which was attributed to the formation of humic-like substances. [The amino groups of aminoalkylalkoxysilanes can be expected to undergo Maillard reactions with carbohydrates and other components of paper, which are similarly expected to increase the acidity of the paper (Kelly, 1979; Tanaka, 1993; Painter, 2001; De La Orden, 2002; Nursten, 2005; and Davidek, 2008).] The article was published by the Mineralogical Society of Great Britain and Ireland with anonymous peer review.


Researchers at the Departamento de Química Orgánica, Universidad Complutense de Madrid (De La Orden) and the Departamento de Ingeniería Química Industrial y del Medio Ambiente, Universidad Politécnica de Madrid (Matías and Martinez) studied the reaction between cellulose and polyethyleneimines (PEIs), which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). The PEIs reacted with cellulose functional groups via Maillard and other possible reactions, which resulted in yellowing. [The amino groups of aminoalkylalkoxysilanes can be expected to undergo Maillard reactions with carbohydrates and other components of paper, which may account for the yellowing of paper treated with aminoalkylalkoxysilanes (Kelly, 1979; Tanaka, 1993; Painter,
The article was published in a Wiley journal with anonymous peer review.


Researchers at the Centre de Recherches sur la Conservation des Documents Graphiques (CNRS, France) studied the impact of spraying Whatman filter paper and an acidic mechanical pulp paper with CSC Booksaver® spray by testing both using exposure to a pollutant, NO₂ (nitrogen dioxide). It was recommended that the spray only be used in a chemical fume hood because of the propanol. It was not easy to control the amount of solvent sprayed. Spraying both sides of paper was not recommended because this soaked the paper and resulted in alkaline reserve values that were too high. No relationship was found between paper pH and either alkaline reserve or the degree of cellulose polymerization of treated vs. untreated papers. Printing ink from one side of the paper transferred to the other side. [It is not clear why the pollution tests were conducted using papers that had been sprayed on both sides of the paper, instead of on only one side, particularly because the authors stated that spraying on both sides was not recommended. Thus, the pollution studies were not conducted using realistically treated papers.] The article was published in a journal with no anonymous peer review.


Researchers in the Department of Chemistry, University of Florence (Giorgi, Dei, and Baglioni); at the Textile Finishing Company (Ceccato), Prato; and a book and paper conservator (Schettino) describe the use of nano particles of calcium hydroxide in 2-propanol as a deacidification reagent. Eighty percent of the particles were 160-380 nm in diameter, with an average size of 260 nm. Scanning electron microscopy showed that the particles were bound to the surface of cellulose fibers in treated paper. The dispersion in 2-propanol was claimed to be harmless to inks and ionic substances. Less than two weeks was needed for the calcium hydroxide in deacidified paper sheets to be converted to calcium carbonate under natural aging. The treatment was shown to prevent the discoloration of paper under artificial aging. The article was published in an ACS (American Chemical Society) journal with anonymous peer review.


Researchers at the National and University Library (Malesic and Kolar) and the Department of Chemistry and Chemical Technology (Strlič), Slovenia, used artificial aging to study the effect of deacidification with magnesium Mg(II) and calcium Ca(II) carbonates on the degree of polymerization (DP) of bleached pulps and papers (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavrilii et al., 2001; Mordasini et al., 2003; Strlič et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). For bleached pulps, Mg(II) carbonate resulted in an initially higher paper pH that correlated with a higher decrease in DP (higher degradation). In contrast, the DP for bleached pulp papers treated with either of the carbonates was the same. [Unfortunately, the pH of all the bleached pulp papers after deacidification was ~ neutral, so the data do not address whether DP was related to the final pH of the papers or a different variable.] For pure cellulose papers, the pH was notably higher using Mg(II) carbonate, but for them, the pH did not impact DP. Results from bleached pulps of different carbonyl content suggested that carbonyl groups might be responsible for the difference in pH sensitivity of bleached pulps (high carbonyl content) vs. cotton papers (low carbonyl content). [The Mg(II) carbonate deacidification solution was four times more concentrated (molar) than the calcium carbonate solution, and how this might have impacted the results was not addressed.] The article was published in a journal with no anonymous peer review.

A Library Counselor in the Acquisitions Department of the National Diet Library, Japan, describes pH surveys of materials dating from 1986-2002 printed in Japan. In 1986, the use of acid-free paper for commercial publications was 51%; in 1990, it had risen to 74%; and it remained steady at ~80% afterwards. However, for official publications, the use of acid-free paper was less: 32% in 1986, and not exceeding 80% until 2002. The occurrence of acid-free recycled paper in government publications began to be surveyed in 1997, and its use grew from 6.3% in 1997 to 16% in 2001. Issues with recycled paper included increase in impurities, decrease in initial strength (shortening of pulp fibers, increased fine particles, accumulated fillers/powders), decrease in brightness (residual inks), decreased pH (slightly acid to neutral), and decreased ability to change in response to the environment (moisture absorption and desorption). The article was published in a newsletter with no anonymous peer review.


A consultant in preservation and collections management describes the INFOSAVE Project to address acidic paper and mass deacidification needs in the UK and Ireland (Rhys-Lewis, 2002a; Rhys-Lewis and Walker, 2003). Conclusions were that there was a significant need for mass deacidification in the UK and Ireland; that a regional structure would be the most effective arrangement for a mass deacidification program; that a collaborative approach to assessing need and developing programs was possible; that mass deacidification was supported in principle throughout the professional sector; that significant material was at risk across libraries, archives, and museums; and that it was vital to continue to promote the INFOSAVE project and its findings. The key recommendations were that the National Preservation Office should be responsible for developing a program to establish a mass deacidification facility to serve the UK and Ireland, as part of the national preservation strategy; that a demonstrator project be conducted; that further collaborative regional surveys be performed to further define the extent of acid deterioration; that proposals for continuing development of the program should be compiled and new funding models investigated. The final INFOSAVE report contains results from a comparison of several mass deacidification processes (Rhys-Lewis and Walker, 2003). The article was published as a report with no anonymous peer review.


This Screening Information Data Set (SIDS) for High-Volume Chemicals is useful for understanding the chemistry of deacidification using carbonates and bicarbonates (hydrogen carbonates), which are the neutralizing components in most mass deacidification processes. When a bicarbonate is added to water, reversible pH-dependent chemical equilibria are established that primarily involve carbonate ions (the major species at alkaline pH > 10.33) ⇌ bicarbonate ions (the major species at more neutral pH 6.35-10.33) ⇌ dissolved carbon dioxide (major species at acidic pH < 6.35). A saturated bicarbonate solution has a slightly basic pH of 8.34. [When the bicarbonate ions react with acids in paper, carbon dioxide is formed and some escapes into the environment. This drives the carbonate ⇌ bicarbonate equilibrium reaction toward the right, converting carbonate to bicarbonate, which keeps the pH at a constant buffered value of 8.34. If too much acid is present so that all the carbonate and bicarbonate are consumed, carbon dioxide becomes the major species and the pH drops below 6.35. Conversely, if the pH is artificially raised above 10.33 by adding hydroxides, the more basic carbonate dominates. By adjusting the pH and amount of carbon dioxide in solution, the chemistry can be controlled so that the less aggressive bicarbonate is the major species that is active in deacidification.]

The Head of Conservation Services, Preservation Division, University of Michigan Library, provides background to the need for mass deacidification, a brief discussion of the Papersave® (Battelle) and Bookkeeper® processes, and a more detailed discussion of the mass deacidification program at the University of Michigan. Specific retrospective book collections were treated, not including rare and special collections. Using the Bookkeeper® process, pre-selection for sensitive inks or cover materials was not necessary; papers that broke with two double-folds were considered strong enough for the process, but papers that broke with one double-fold were not. Books were off the shelf for 4-6 weeks; staff time for processing was ~ 2.25 minute per book; ~ 275 books were shipped every two weeks; treatment costs including vendor, shipping, and library staff were ~ $16 per volume. It was concluded that mass deacidification was one option for book deterioration problems and had a place in a comprehensive preservation program. The article was published in a newsletter with no anonymous peer review.

2001


A researcher at the Schweizerische Landesbibliothek SLB (Blüher) and staff from Nitrochemie Wimmis AG (Vogelsanger), the operator of the Papersave® Swiss deacidification plant, review mass deacidification with a focus on Papersave® Swiss. Useful tables summarize different processes and ingredients. Alkaline magnesium Mg(II)-based reagents predominate. Aqueous methods (Neschen (Bückeburg)) were suitable for treating single sheets, but inks and dyes bled. Non-aqueous processes that used non-polar solvents and dissolved reagents (CSC Booksaver®, Papersave® Battelle) required predrying, which was physically stressing to paper, leather, and parchment. Treatments that used fine particles and no drying (Bookkeeper®, Libertec®, SOBU) permitted treatment of leather and parchment, but it was inferred that microparticles did not penetrate paper fibers as well as dissolved reagents. Papersave® Swiss, the third generation Battelle process, used magnesium titanium ethoxide in hexamethyldisiloxane. The process resulted in yellowing and darkening during treatment, but the color change of treated papers was less than untreated papers during artificial heat aging. Homogeneous distributions of 0.5-2% alkaline reserve and pH values >7.0 were achieved. Some red inks were unstable, so parchment, leather, and some red-covered books were not treated. The article was published in a journal with no anonymous peer review.


This patent is for using aminoalkylalkoxysilanes as mass deacidification reagents (Cheradame 2003, 2004, 2005, 2006a, 2006b, 2008). The premises were that aminoalkylalkoxysilanes either would bond directly to the paper via silanization reactions or self-condense to form a polymeric coating, both of which were claimed to leave the amino groups free to neutralize acids in the paper. Acidic papers were immersed in solutions of aminoalkylalkoxysilanes in aromatic (toluene and xylene), ketone (acetone and methylethylketone), ester (ethyl acetate), and alcohol (ethanol, methanol, and isopropanol) solvents and dried at temperatures up to 90 °C to accelerate the polymerization reaction and simultaneously remove the solvents. Solutions of 6-12% provided enough alkalinity to neutralize paper acidity, but these concentrations did not provide enough alkaline reserve (AR) for permanence [i.e., the remaining AR after neutralization of the initial acidity was < 1.5% CaCO3 equivalent].


Researchers in the Department of Chemical Engineering at the Complutense University of Madrid (Dufour) and at the TNO Institute of Industrial Technology in The Netherlands (Havermans) report
results from intense artificial light aging of acidic mechanical pulp papers treated using Papersave®, Bookkeeper®, diethylzinc (DEZ), FMC-Lithco-MG3, and Sablé mass deacidification processes. Error bars were not provided for the FTIR data, and no spectra were provided. Most of the FTIR data for all processes were the same +/- 20% except for the FMC process, which appeared to cause a statistically significant oxidation/degradation of the paper both before and after light aging. The errors in the folding endurance data were in some cases +/- 50%, and the number of samples analyzed was not provided, so it is difficult to statistically analyze the data. The article was published in a journal with no anonymous peer review.


Researchers at National Silicates provide a good summary of issues involved with transition metal-ion catalysis of cellulose oxidation and its inhibition by the addition of magnesium Mg(II) salts, which is relevant for understanding the impact of Mg(II)-containing deacidification reagents on paper (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Malesic et al., 2001; Mordasini et al., 2003; Strlič et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójcik, 2006; Logenius et al., 2008). Hydrogen peroxide formed during air oxidation was unstable in the presence of transition metal ions, mainly manganese Mn(II), iron Fe(III), and copper Cu(II), and decomposed to give hydroxyl free radicals that in turn oxidized cellulose. Mg(II) salts inhibited the oxidation by the formation of magnesium hydroxide at high pH, which bound the transition metal ions via oxo or hydroxo bridges to prevent them from undergoing oxidative electron-transfer reactions. It was important for the Mg(II) salts to dissolve first and penetrate the fibers prior to being precipitated as magnesium hydroxide so that the transition metals occurring naturally in the fiber interiors could be accessed and deactivated. A large amount of data were given that show the relationship between peroxide levels, brightness, delignification, viscosity, and physical parameters (zero span, strength) on the Mg(II) loading. The article was published in conference proceedings with no anonymous peer review.


This patent is for a process by which a deacidification reagent contained in a polymeric enclosure gradually migrates to acidic paper from either a reservoir and/or carrier material. The polymer itself could be the source of deacidification reagent by containing an additive in the enclosure film or an additive in a coating on the enclosure film. One specific example was the use of an amino-functional dimethylsiloxane as deacidification reagent, as in the articles by Cheradame (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). Another example was the use of organic amines. Problems with some amines included their irritating vapors, their cause of skin sensitization problems, and the fact that they cause the paper to discolor [similar to discoloration of papers described in the Cheradame articles perhaps a result of Maillard reactions (Kelly, 1979; Tanaka, 1993; Painter, 2001; Bosetto, 2002; De La Orden, 2002; Nursten, 2005; and Davidek, 2008)]. The solvents used were hexane or heptane in cases in which the papers were immersed in solutions of the silanes. Problems included the permeability of the polymeric enclosures to amines so that in some cases, the amines were lost over time to the environment.


This monograph by a consultant previously employed by the DuPont Company contains chapters on structure, synthesis, physical and chemical properties, analysis, and other features related to perfluorinated surfactants, which is relevant for understanding the chemistry and environmental impact of the surfactant used in the Bookkeeper® deacidification process (Leiner and Kifer, 1993; Leiner et al., 1998; Leiner et al., 2000; Zumbühl and Wuelfert, 2001; Järnberg and van Bavel, 2006; Guo et al., 2008). The anionic perfluoropolyether acid surfactant used in Bookkeeper® helps keep the magnesium oxide particles dispersed in the perfluoroalkane solvent. The surfactant would have a pKa of ~ 1.7 (a strong acid) and a critical micelle concentration in the micromolar range, which would enable it to be
used at low concentrations. [The Bookkeeper® surfactant should be more biodegradable because of its ether linkages, and its biodegradation products should result in short-chain perfluorinated compounds that would not bioaccumulate and would not be biopersistent. In addition, approximately 99% of the surfactant remains in the paper after deacidification treatment, so its emission into the general environment would be minimal.]


The head of the Technical Department, University of Mainz, Germany, discusses results from the Papersave® (Battelle) process. The life expectancy of an acidic, non-brittle newspaper was increased by a factor of four by deacidification, but a brittle newspaper needed the paper-splitting process to make it usable. The increased strength of the deacidified non-brittle newspaper was independent of alkaline reserve (AR) in the AR range of 0.6-4% magnesium carbonate, but for the brittle paper, increasing the AR above 1% caused a significant loss in strength, which was attributed to an increased stiffening of the paper. Samples from books deacidified in 1995 and stored in a standard climate were tested in 1995, 1998, and 2000 with no diminishment in treatment effects over the five-year period. It was recommended (1) that mechanically sound high-risk materials be deacidified as soon as possible, because deacidification results are significantly better for paper that is still in good condition, and (2) that the AR be adjusted in relation to the starting quality of the paper being deacidified. It is notable that surface pH had the lowest relevance in relation to paper condition in the natural aging studies. The article was published in an IADA (Internationale Arbeitsgemeinschaft der Archiv-, Bibliotheks- und Graphikrestauratoren, or International Association of Archive, Book and Paper Conservators) journal with anonymous peer review.


The Training and Development Officer, Conservation Department, British Library summarizes presentations made at a mass deacidification conference organized by the European Commission on Preservation and Access (ECPA) and sponsored by the company that provides the Neschen (Bückeburg) mass deacidification process. Abstracts from the conference can be found at http://www.knaw.nl/ecpa/conferences/abstracts-e.html#1. Presentations addressed how specific processes were selected, how the processes worked, and how collections were selected for mass deacidification. Overall, in practice, each process performs in a specific way and some have negative side effects on different types of materials. The article was published in a newsletter with no anonymous peer review.


In this monograph chapter, a professor in the Department of Biotechnology, Norwegian University of Science and Technology describes how carbohydrates in Sphagnum mosses, which include galacturonic acids, undergo spontaneous Maillard reactions with ammonia and other amines to produce brown polymers, which is background chemistry for the proposed use of aminooalkyalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). These reactions occur at a higher rate because the ketouronic acids are more unstable than other sugars. [The amino groups of aminooalkyalkoxysilanes can be expected to undergo Maillard reactions with carbohydrates and other components of paper, which might explain the discoloration of paper treated with aminooalkyalkoxysilanes (Kelly, 1979; Tanaka, 1993; Bosetto, 2002; De La Orden, 2002; Nursten, 2005; and Davidek, 2008).]


A consultant in preservation and collections management presents results of a feasibility study for the
INFOSAVE Project that addressed acidic paper and mass deacidification needs in the UK and Ireland. A useful table compares the cost per volume of binding/boxing ($6.00), deacidification ($15.50), microfilming ($135.00), simple ($500.00) and complex ($1900) digitization, and conservation ($2000) at the Library of Congress. A graph is given of similar costs at Yale University. Detailed results from a questionnaire/survey were given along with useful summaries of the different mass deacidification processes. More information is given in the second-phase report (Rhys-Lewis, 2002b), and the final INFOSAVE report (Rhys-Lewis and Walker, 2003) gives results from a comparison of several mass deacidification processes. The article was published as a report with no anonymous peer review.


A staff member of Neschen UK Ltd., Staffordshire, UK, describes a new plant for aqueous mass deacidification of documents using the Neschen (Bückeburg) process. Documents were deacidified and strengthened by the use of methylcellulose in conjunction with magnesium bicarbonate. Brittle documents were treated by hand. The article was published in a newsletter with no anonymous peer review.


Scientists at the Art Technical Laboratory of the Technical University of Applied Sciences of Berne describe results from using x-ray diffraction (XRD), energy-dispersive x-ray fluorescence spectroscopy (XRF-EDS), Fourier transform infrared spectroscopy (FTIR), and polarized light microscopy to study products remaining on various substrates after use of Bookkeeper® spray. The perfluorinated carboxylate surfactant remained on all substrates including cellulose filter paper after 12-18 months of storage under normal ambient conditions (Leiner and Kifer, 1993; Leiner et al., 1998; Leiner et al., 2000; Kiss, 2001; Järnberg and van Bavel, 2006; Guo et al., 2000). Although hydrolysis of MgO could not be monitored by FTIR, bands from magnesium hydroxide disappeared as bands from magnesium carbonates appeared. The rate of formation of carbonates was substrate dependent, with cellulose slowing a slower rate. The water-repellent fluorinated surfactants adsorbed on the surface of the MgO particles were suggested to slow down the rate of hydrolysis and conversion into carbonates. The carbonate species formed were not pure carbonates (i.e., nesquehonite, hydromagnesite, or artilnite) but appeared to be co-crystals with fluorinated materials. The article was published in an IIC (International Institute for Conservation) journal with anonymous peer review.

2000


A researcher at the Slovak National Library describes results from studying the effect of deacidification on the photooxidation of modern and historic groundwood newsprint paper, and Whatman 100% cellulose paper. Papers were deacidified using 4% magnesium methyl carbonate (MMC) in methanol. Samples were placed on a windowsill in direct southern, summer sunlight that was UV-filtered by double-paned window glass for 156 days. Deacidification with MMC without light aging resulted in an increase in pH and alkaline reserve but a decrease in double folding endurance and brightness (increase in yellowing) for all but the Whatman paper. With light aging, all treated newsprint papers had reduced folding endurance compared to untreated papers except for one modern paper, but treated Whatman paper had increased folding endurance after aging. Deacidification reduced the formation of carbonyls both before and after aging in comparison to non-treated papers [suggesting that hydrolysis was reduced because of deacidification]. However, there was an increase in carbonyls overall for both treated and untreated papers, and this increase was believed to be at least partially responsible for the decrease in folding endurance. [The data suggest that lignin and/or other non-cellulosic materials, which could include transition metal ions, in the newsprint papers were primarily responsible for their photooxidation (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic and

Researchers from De Montfort University, UK, (Bülow); the Canadian Conservation Institute (Bégin); the Augustana University College, Canada, (Carter); and Queen's University, Canada, (Burns) describe results from artificial hydrothermal aging of papers in stacks, which models sheets in books, to evaluate the impact of migration of volatile acidic degradation products from papers internal to the stack to external papers. Yellowing increased and pH decreased from the top of the stack to the middle, indicating that volatile acidic degradation products were trapped towards the center of the stack but were able to escape into the environment from the outer sheets. [The data suggest that mass deacidification of books and other materials, such as manuscripts, stored in stacks would be particularly useful for neutralizing and absorbing the volatile acids to minimize their impact on degradation rates.]

Zero-span tensile strength was not a sensitive or reliable indicator of cellulose degradation because it was only related to the degree of polymerization (DP) of the cellulose after the paper had significantly degraded. The article was published in a journal with no anonymous peer review.


The Chief of the Document Conservation Laboratory at the US National Archives and Records Administration (NARA) describes the differences between archives and libraries in regard to loose and bound materials. These differences include the uniqueness of each record at an archive, and the generally better paper. At NARA, improvement of environmental storage conditions, microfilming, and improving the quality of new records have been the major preventive conservation focus as opposed to mass deacidification. The article was published in conference proceedings with no anonymous peer review.


Researchers in the Conservation Processes and Materials Research Division of the Canadian Conservation Institute describe results from experiments to study the artificial hydrothermal aging of acidic softwood and chemithermomechanical pulp paper and to develop a new artificial aging test. The work provides background to the chemistry and methods that are typically used to study the stability of deacidified and other papers. Pertinent findings were that the moisture content of paper is an important variable that impacts results from Arrhenius studies, so it is important to increase the relative humidity with the temperature so that the moisture content remains the same at all temperatures; papers in stacks aged faster than papers as free-hung sheets; Arrhenius plots of cellulose depolymerization gave activation energies ($E_a$) comparable to those from other types of studies; different papers gave different relationships between their physico-mechanical properties and the degree of polymerization of the cellulose in the paper; and a new artificial aging test protocol was developed in conjunction with researchers at the Library of Congress (Shahani et al., 2002) that better mimics natural aging. The article was published as a report with extensive peer review.


This patent is an improvement upon a previous patent that describes the use of hydrofluoroether carriers.
carriers in the Bookkeeper® mass deacidification process. [It is stated that the surfactant evaporates with the carrier, but this is not the case. Approximately 99% of the nonvolatile, high molecular mass (average molecular mass 2000-3000) surfactant is retained in the paper after treatment.]

Porck, H. J.  

A conservation scientist at the National Library of the Netherlands provides an introduction to artificial aging of paper, describes the principles and techniques including Arrhenius artificial aging tests, and discusses the reliability and the predictive use of the results. An extensive bibliography from 1955-1997 is provided. Issues that are still relevant a decade later include that there is not a universally used artificial aging method so data between labs is difficult to compare; data do not provide for absolute determinations of paper degradation rates but only relative rates; and high temperature aging may not reflect natural aging [but see Shahani et al., 2000, in which closed-tube aging data were interpreted to reflect natural aging]. Paper decomposes via three natural mechanisms: acid-catalyzed hydrolysis by water, oxidation by oxygen, and thermal degradation. To extrapolate results from Arrhenius rate experiments, which measure a change in a material over time with increasing temperature, to ambient temperature, all three mechanisms must either have rates that are accelerated in the same proportion across all temperatures, or the average of their rates must change by the same factor across all temperatures. The article was published as a report with multiple peer review.

Porck, H. J. and R. Teygeler.  

Researchers at the Koninklijke Bibliotheek, The Hague, Netherlands, provide a comprehensive overview of the status of preservation research regarding paper, film, photographic, and magnetic tape collections; general storage issues; and treatments, including mass deacidification, as of 2000. Many of the research needs of 2000 are still in existence today. For paper, research needs of 2000 included foxing, ink corrosion, and tide lines; the need for suitable instruments for diagnosing the state of paper deterioration that can test a large number of samples in a short period of time; the impact of deacidification on thermal and photo-oxidation processes; laser cleaning; natural insecticides; and the reinforcement of deteriorated paper objects on a large scale. Mass deacidification was acknowledged as being an integral part of mass preservation strategies. The article was published as a report with peer review.


The Chief of Preservation Research & Testing at the Library of Congress and coworkers describe results from experiments to study the artificial aging of paper in terms of mechanical properties and chemical degradation products, and to develop a new artificial aging test. The work provides background to the chemistry and methods that are typically used to study the stability of deacidified and other papers. Some notable results were that the relative humidity must be increased while increasing the temperature during Arrhenius artificial aging studies to keep the equilibrium moisture content of the paper the same in all the experiments (Kaminska et al., 2002); the presence of calcium carbonate reduces the equilibrium moisture content of paper; the activation energy (Eₐ) determined from Arrhenius plots of decomposition rates of papers with different physicochemical properties varies widely and depends on method of aging and type of paper; organic acids are formed during the aging of paper independent of paper type and paper pH; and water- and methanol-soluble products formed from artificial aging inside sealed glass tubes, determined by ion chromatography and capillary
electrophoresis, appear to be similar to products formed from natural aging. The article was published as a report with extensive peer review.


This patent is for the improvement of the Wei T'o® deacidification apparatus and methods that involve solutions of organic multi-valent metal carbonates, low-moisture alcohols (from methanol to butanol), and other low-moisture solvents including alcohols, aliphatic hydrocarbons, fluorocarbons, and blends thereof. Aerosol sprays contained hydrofluorocarbons (HFCs).


The Preservation Policy Officer of the State Training School for Conservators, Amsterdam, describes the approach for selecting Bookkeeper® as the mass deacidification process for use at the Dutch State Archives. It began with a damage survey that showed that the most threatened collections were from 1840-1950, with the worse cases from 1870-1880. The first process studied was diethylzinc (DEZ), but with its commercial termination, the only two available alternatives were Papersave® (Battelle) and Bookkeeper®. Bookkeeper® was selected over Papersave® because the Papersave® (Battelle) process left a residue of silicon oil, caused an initial loss of strength (up to 40%), printing inks were affected, and there was no trace of paper strengthening. Details are provided of the logistics and a more general approach for selecting collections to deacidify. The article was published in conference proceedings with no anonymous peer review.

1999


Researchers at the Canadian Conservation Institute (CCI) report results from studies of the physicochemical properties of naturally aged brittle book papers from the mid-19th to early 20th centuries, from artificial hydrothermal aging of papers in stacks compared to single sheets suspended in an oven, and from artificial hydrothermal aging of papers mass deacidified using diethylzinc (DEZ), Wei T'o®, and the FMC-Lithco-MG3 process. The pH, moisture content, and strength of lignin-containing naturally aged papers were significantly less than non-ligneous naturally aged and unaged modern papers. Artificial hydrothermal aging of papers in stacks, as opposed to hanging free in an oven, caused the accumulation of acidic decomposition products so that the papers degraded in a manner that more closely reflected natural aging. The three mass deacidification processes all improved paper strength, and the treatments particularly improved the strength of papers aged in stacks. An important observation was that zero-span breaking length was not a good indicator of the rate of paper degradation because it did not relate to degree of polymerization of the cellulose. The article was published in conference proceedings with no anonymous peer review.


A researcher at the Slovak National Library describes research aimed at determining the amount of damage caused by oxidation vs. acid hydrolysis of modern and historic groundwood containing deacidified newprint. Control samples were soaked in methanol; deacidified papers were soaked in a 4% solution of magnesium methyl carbonate (MMC) in methanol. Dry-heat artificial aging was conducted at 103 °C for 12 days, which would have significantly reduced the moisture content of the paper. Tests included microscopy, double folds, brightness, pH, optical density of an extract, hydrazine determination of carbonyl content, methylene blue determination of carboxyl content, and Klason lignin. Modern papers had longer fibers than historic papers. Deacidification with MMC without artificial aging
resulted in an increase in pH and alkaline reserve but a decrease in double folding endurance and a
decrease in brightness (increase in yellowing). With artificial aging, modern treated papers were able
to maintain much of their non-aged folding endurance, but historic papers lost their folding endurance
after 3-6 days of aging. Deacidification reduced the formation of carbonyls in treated compared to non-
treated papers [suggesting that hydrolysis was reduced because of deacidification]. The article was
published in a journal with no anonymous peer review.

Drewes, J. and K. Smets. "Deacidification of Journals— Saving the Past and Present for the Future." In
(accessed April 9, 2010).

This bibliography by the Assistant Director for Access and Preservation, Michigan State University
Library (Drewes) and the Monograph Copy Cataloging Coordinator, Milton S. Eisenhower Library,
Johns Hopkins University (Smets) provides a bibliography of 20 references from the years 1991-1997
related to mass deacidification.

(accessed August 24, 2010).

Researchers at the US National Cancer Institute provide a good introductory explanation of metal ion
chemistry, which is relevant background for understanding the impact of calcium Ca(II)- and
magnesium Mg(II)-containing deacidification reagents on paper and paper decomposition (Corbett,
1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and
van Damme, 1990; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Strlič et al.,
2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). The chemistry of ligands,
icoordination and coordination spheres, and charge distribution and its impact on the stabilization of the
reaction transition state is discussed. The chemistry of Mg(II) and Ca(II), which is not the same, is
compared to manganese Mn(II), zinc Zn(II), and lead Pb(II). The concept of hard and soft acids and
bases is explained in an easily understood manner. The article was published in a journal with no
anonymous peer review.

Hofenk de Graaff, J. H. "Waves of Knowledge Trends in Paper Conservation Research." In

A textile chemist at the Instituut Collectie Nederland, Amsterdam, presents a historical essay on paper
conservation. In 1823, an observed decline in the quality of paper was linked to new bleaching
methods, mechanization, and the change from rags to mechanical wood pulp. In 1843, "red rot" of
leather bookbindings was linked to pollution caused by combustion of coal gas, which produced sulfur
dioxide that then reacted with water to give sulfuric acid. Iron gall ink was a noted problem in 1899.
Research conducted in the paper industry was the foundation for the later field of paper conservation,
and paper conservation scientists, such as William J. Barrow, demonstrated for librarians the
contribution of paper acidity and wood pulp to paper degradation. Damage inventories in the late
1900s showed that 40% of 19th century paper was seriously damaged, which lead to the development
of mass deacidification. Much current preservation relies on preventive conservation such as controlled
environments and good storage materials. However, brittle paper, iron gall ink, impact of
microclimates, the predictive value of artificial aging, and others issues were deemed to be still in need
of research. The knowledge transfer between conservation scientists and managers was described as
being slow, which could have resulted in some management decisions being made with basis in
outdated knowledge. The article was published in conference proceedings with no anonymous peer
review.

Kellerman, L. S. "Combating Whole-Book Deterioration: The Rebinding & Mass Deacidification
Program at the Penn State University Libraries." Library Resources & Technical Services
The preservation librarian of Penn State University Libraries, University Park, Pennsylvania, describes logistical and other details of a mass treatment program for older books that were first commercially rebound and then deacidified using the Bookkeeper® mass deacidification process. Rebinding was needed so that the books would be durable enough to withstand the rigors of the process. A survey of books printed from 1990-1992 revealed that 86% were printed on alkaline paper. Of these, 91% of books printed in the US were alkaline, but all books printed in India and Africa were acidic. Older materials printed in the US were primarily acidic. Items that were not considered suitable for treatment included alkaline paper, glossy clay-coated paper, leather covers with red rot, plasticized covers, and brittle paper. Tracking each item sent for treatment enabled patrons to know their availability. The USMARC 583 field was used to report the preservation action in local bibliographic records. Selection criteria were developed. After treatment, the spines of all books were marked with an infinity symbol to provide a quick visual display of books that had been treated. The article was published in a journal with no anonymous peer review.


Researchers at the National and University Library of Slovenia (Kolar) and the University of Ljubljana (Strlič, Novak, and Pihlar) introduce oxidation of paper and describe results from 80 °C, 65% relative humidity (RH) artificial aging of paper under alkaline (deacidification) conditions. Oxidation occurred from reactions between cellulose and primarily hydroxyl free radicals that arose from decomposition of peroxides. Transition metal ions such as cobalt Co(II), iron Fe(II), copper Cu(II), and manganese Mn(II) catalyzed peroxide decomposition (Corbett, 1973; Sinký, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). High pH promoted the ionization of aldehyde (carbonyl) groups in cellulose that made them easily oxidized to initiate autooxidative radical reactions. The use of the chelating reagents EDTA and DTPA to complex transition metal ions to prevent their catalysis had no effect, and the addition of sodium phytate resulted in greater degradation [most likely because of the high pH]. The use of borohydride to eliminate carbonyls at first improved the stability of the paper, but with longer aging, the result was negative [most likely because of the high pH caused by residual sodium borate]. Antioxidants, including iodide that decomposes peroxides to hydroxyl anions instead of hydroxyl radicals, and BHT, a free-radical chain-breaking antioxidant, were effective at protecting the paper, with iodide being superior. The article was published in a newsletter with no anonymous peer review.


This patent is for using solvent-free ultrasound to apply dry metal oxides to paper for mass deacidification. A sheet or book is either immersed in a bed of metal oxide particles that are sonically energized, passed through a zone containing an energized bed of particles, or treated with energized particles that impinge on the object. The sonication frequency is 5 kHz-5 MHz. Sub-micron sized particles in the gas-solid fluidized bed are claimed to penetrate paper fibers better without needing solvents or significant mechanization. [Sonication in liquids is very damaging because of cavitation (microbubble formation and implosive collapse) that can create temperatures of 5000 K, pressures of 2000 atm, intense shock waves in the microenvironment of the bubble, and high particle velocities of 170 m s⁻¹ (half the speed of sound) (Mason, 2009). Sonication of cellulose in water results in its degradation, microfibrils break down into elementary fibrils, and paper is de-inked (Prozorov et al., 2004; Colvin, 1976; Kolpak and Blackwell, 1975). Although the proposed fluidized bed does not use a liquid, and the particle velocities are stated to be between 0.0001-0.1 m s⁻¹, no data are presented that address possible impact on papers, covers, and particularly inks that could suffer mechanical abrasion.]

Mass Deacidification Annotated Bibliography 1990-2010
January 2011
Library of Congress ● Preservation Directorate

www.loc.gov/preserv

This patent is an improvement on a previous patent for the apparatus used in the Bookkeeper® mass deacidification process. The apparatus permits books to be immersed in the treatment reagent in a direction parallel to the book spine and simultaneously sprays the book pages in a perpendicular direction to the spine. Following treatment, excess reagent is removed from the material and recycled.


The editor of a conservation newsletter presents a brief summary of the Vienna mass deacidification process [no longer commercially available]. The procedure involved using an aqueous solution of borate and sodium hydroxide to deacidify, plus methylcellulose to strengthen the paper. Covers had to be removed from bound books before treatment. After treatment, the books were placed under high vacuum and freeze-dried. After treatment, the covers were reattached to the books. The article was published in a newsletter with no anonymous peer review.

1998


A researcher at the Institut für Buch- und Handschriftenrestaurierung der Bayerischen Staatsbibliothek, Germany, presents results from artificial aging of historic and modern papers deacidified using aqueous solutions of magnesium bicarbonate or calcium bicarbonate. Dry and moist heat aging was performed, and the papers were tested for alkaline reserve, yellowing, brightness, mechanical strength, and surface pH. [Much of the data contains a high amount of scatter, there are too few data points in the plots, and contradictory findings are not explained. The amount of magnesium bicarbonate in the papers was significantly greater than the amount of calcium bicarbonate, as was the pH of the magnesium-treated papers, factors that could account for the greater yellowing [alkaline darkening] that occurred with magnesium bicarbonate. The data were not analyzed or interpreted in relationship to previous studies including those that suggest that the high level of iron present in the historic papers could have caused transition-metal catalyzed oxidation under the humid oven aging conditions, which might have been partially inhibited by the presence of magnesium, and which could account for some of the data (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Strlič et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008).] The article was published in a journal with no anonymous peer review.


Researchers at the Universitat Politècnica de Catalunya, Escola Tècnica Superior d'Enginyers Industrials, Spain, investigated the impact of alkoxypolyethylene glycols (ALKPG) on the strength of paper to determine if ALKPG magnesium compounds could be used as a simultaneous paper deacidification and strengthening reagent. The ALKPG compounds remained permanently within the paper after drying and were not easily removed after washings. There was a dramatic loss of mechanical strength after treatment so that these types of compounds were not suitable for paper deacidification/strengthening. The article was published in a journal with no anonymous peer review.


Conservators at the Library of Congress evaluated Bookkeeper® spray for deacidifying single sheets from books. There was no relationship between surface pH and alkaline reserve (AR) for different
levels of spray. Papers impregnated with Brilliant Yellow dye were sprayed, and the color change from yellow (acidic pH < 6.6) to orange (alkaline pH > 7.8) did not occur until the papers were humidified. [This result is not surprising because pH-indicating dyes must have sufficient water present so that ionization and the resultant color shift can occur. Further, the mechanism of adsorption of direct substantive dyes such as Brilliant Yellow to paper involves hydrogen bonding of their phenolic groups to cellulose, which prevents their ionization and the resultant color shift under more anhydrous conditions (Tímár-Balázsy and Eastop, 1998; Amelin and Tretyakov, 2003; Strlić et al., 2004b; EMD Chemicals, Inc., 2005; Polymathic Analytical Labs, 2009). Further, Brilliant Yellow changes color from yellow to red not from alkalinity but from chelation of magnesium Mg(II) (Taras, 1948).] The AR was shown to penetrate into a second layer of newsprint paper and into four layers of Japanese paper. Bookkeeper® was deemed suitable for all materials tested except for slick or highly calendared papers, black or dark-colored papers, and media and polymers that needed to be first tested for pH sensitivity and solubility. The article was published in conference proceedings with no anonymous peer review.


This patent is to use hydrofluoroether solvents instead of perfluorocarbons (PFCs) in the Bookkeeper® deacidification process. One solvent is 3M® Novec® HFE7100, which is a mixture of two methoxy-nonfluorobutane isomers (C₄F₉OCH₃, CAS numbers 163702-08-7 and 163702-07-6). The benefit of replacing PFCs with short-chain hydrofluoroethers is that PFCs have a high global warming potential (GWP), ~ 7000 times that of CO₂. In contrast, HFE7100 has a GWP that is ~ 320 times that of CO₂. A perfluoropolyoxyether alkanoic acid surfactant (Fomblin® monoacid, average molecular mass 2000-3000) was used to keep the particles of magnesium oxide dispersed in the solvent. [The non-volatile surfactant remains in the paper after treatment.] Examples are given in which the ratio of the amount of magnesium oxide to surfactant was ~ 4:1. If the initial mass of the paper were 4.5 grams, and 99% of the surfactant were retained in the paper after deacidification, a spray treatment using a solution of 0.25% magnesium oxide and 0.075% surfactant to give an alkaline reserve of 1.6% would result in the deacidified paper containing 0.7% MgO and 0.2% surfactant.


Information contained in various chapters in this monograph by the Head of the Faculty of Object Conservation, Hungarian National Museum and Hungarian Academy of Fine Arts (Tímár-Balázsy) and a Senior Lecturer at the Textile Conservation Centre, UK (Eastop) provides insight into the physicochemical properties of dyes adsorbed onto cellulose. This is relevant for understanding why using the color change of Brilliant Yellow dye as a test of the deacidification efficacy of the Bookkeeper® processes is not a valid indicator of pH (Kidder et al., 1998). In particular, direct substantive dyes such as Brilliant Yellow pH indicator bind to cellulose via van der Waals forces in addition to hydrogen bonding between the color-change inducing phenolic groups in the dye and hydroxyl groups on the cellulose. This hydrogen bonding “fixes” the dye to the paper so that the phenolic groups cannot dissociate to give a color change unless enough moisture is present to solvate them, facilitating their ionization (dissociation), thus breaking the hydrogen bonding (Taras, 1948; Amelin and Tretyakov, 2003; Strlić et al., 2004b; EMD Chemicals, Inc., 2005; Polymathic Analytical Labs, 2009). [This is why Brilliant Yellow and similar dyes absorbed onto paper prior to a non-aqueous deacidification treatment would not be expected to change color to indicate the extent of deacidification until the paper was exposed to high humidity.]

1997


This article by a Public Affairs Office intern at the Library of Congress summarizes the choice and use of the Bookkeeper® process for the Library’s mass deacidification program. The process uses a
nonaqueous solvent that contains dispersed particles of magnesium oxide to neutralize paper acidity and leave an alkaline reserve. Millions of the Library's books were stated to be in danger of destruction because of being printed on acid paper, and the mass deacidification program was designed to alleviate this problem. The article was published in a newsletter with no anonymous peer review.


A researcher at TNO Institute of Industrial Technology, Delft, The Netherlands, provides a literature review that summarizes the Bookkeeper® mass deacidification process, how it differs from others of the time, and results from tests conducted by others. The article was published as a report with no anonymous peer review.


A staff member at the National Diet Library, Tokyo, Japan, discusses the impact of deacidification on new and old papers. Both new and old papers benefited significantly from deacidification. The mass deacidification process used in the work was ammonia-ethylene oxide [no longer commercially available]. The article was published in a journal with no anonymous peer review.

**1996**


A scientist at Augustana University College, Camrose, AB, Canada, introduces the general chemistry of mass deacidification methods available at the time: diethylzinc (DEZ), Wei T'o®, FMC-Lithco-MG3, Bookkeeper®, Viennese, Book Preservation Associates (BPA), Sablé, and Papersave® (Battelle) with 84 literature references. Results from a number of comparative studies were discussed, all of which are reviewed in this annotated bibliography. [Of the processes described, only Bookkeeper® and Papersave® are currently commercially available mass deacidification options]. The article was published in an ACS (American Chemical Society) journal with anonymous peer review.


Researchers from the TNO Centre for Paper & Board Research (Havermans and van Deventer) and the National Library of the Netherlands (Pauk and Porck) studied the Papersave® Battelle process. Treatment resulted in inhomogeneous coverage, odor, Newton rings, ink and dye bleeding, discoloration, and a "glassy" feeling from residual silicon compounds. A large percentage of books had a significantly lower folding endurance and/or tear resistance after treatment, and the inference was that it was caused by a negative effect on the paper sizing. However, after artificial heat aging, the majority of treated books had less of a strength decrease than untreated controls. Artificial heat aging did not cause the pH of treated materials to decrease from their alkaline pH value of 9.3, but exposure to SO₂ and NO₂ followed by heat aging caused a decrease in pH from 9.3 to neutral 7.0. At the same time, aging of treated papers resulted in a significantly higher paper strength than untreated controls. The alkaline reserve was distributed between the fibers, comparable to normal paper-filling chemicals. The shortcomings of the process were deemed prohibitive to large-scale application. The article was published as a report with no anonymous peer review.


This patent describes the apparatus for the Bookkeeper® mass deacidification process. It consisted of a tank with holders for multiple books, spray of the reagent to better reach the paper near the spine,
and a method for recycling the solvent.


A researcher at the Centre of Preservation and Conservation, German Library (Liers) and staff from Battelle Ingenieurtechnik, Germany, (Wittekind and Theune) describe the Papersave® Battelle mass deacidification process. The effectiveness was evaluated by treating a 20-year old, rosin-sized, acidic (pH 4.9), wood-based, test paper. The process resulted in a final pH of 8-9 and an alkaline reserve of 0.71% magnesium Mg(II) carbonate. Artificial hydrothermal aging resulted in the pH of the paper decreasing over time to a neutral pH of 7, and the alkaline reserve decreasing to 0.25%. The process increased the tensile strength of the paper both before and after hydrothermal aging [suggesting the paper became more brittle]. Leather samples were degreased by the process, which resulted in a decrease of softness and flexibility. The flexibility of new leathers was considered acceptable after treatment, but old leathers became so brittle they broke under bending. [A later study (Larsen, 2005) indicated that Papersave® negatively impacted new and old leathers. The study did not address the impact of the process on inks, which Buisson (2004 and 2006) later showed was negative in some cases.] The article was published in conference proceedings with no anonymous peer review.


Researchers at the Pulp and Paper Institute of Canada (Middleton, Scallan, and Zou) and the Institute of Paper Science and Technology, USA (Page) used high pressure (350 kPa or 50 psi) and humidity (97% relative humidity, RH) to deacidify acidic sheets in contact with sheets that contained high quantities of highly insoluble calcium carbonate, and present data that are significant in regard to nonaqueous mass deacidification processes. The rate of deacidification of bound acidic groups, such as oxidized groups in lignocellulose, using inorganic alkaline reagents, such as calcium carbonate, was predicted to be very slow (many years) at typical ambient humidities because there was not enough unbound water in the paper even at 50% RH to solubilize the reagent to allow ionization and subsequent neutralization. However, the greater the solubility of the reagent, the faster the rate. [Conversion of magnesium and calcium deacidification reagents into their more soluble bicarbonates by reaction with atmospheric CO₂ would increase the rate of the neutralization reactions.] TAPPI cold extraction pH measurements and titrations of paper acidity were performed in the presence of 0.1 M sodium chloride to maintain a high ionic strength and obtain more accurate pH data. [By plotting data from Table II, it can be seen that paper acidity has little relationship to paper pH particularly in the acetic acid-acetate buffering region (pH 3-6).] The article was published in a TAPPI (Technical Association of the Pulp and Paper Industry) journal with anonymous peer review.


A scientist in the Library Research Department, Koninklijke Bibliotheek, the Netherlands, presents results from artificial hydrothermal testing of books after deacidification using the Bookkeeper® mass deacidification process. The inside papers contained a white coating of magnesium Mg(II) oxide so that dark pictures in treated books looked lighter than in controls. It was mentioned that since this study, the company has decreased the amount of Mg(II) oxide in the reagent so that this might not be a current issue. The treatment did not cause discoloration, odor, visible Newton rings on pictures on art paper, or physical damage to synthetic bookbinding materials, which were stated to be problems with the Papersave® Battelle process. Bookkeeper® resulted in a decrease in paper strength in 13% of the samples, compared to 41% for the Papersave process. After hydrothermal artificial aging, however, 80% gained significant strength, which was comparable to Papersave®. Papers that significantly improved in strength after aging were those that were rougher and had a lower initial pH before treatment. Artificial hydrothermal aging caused both treated and untreated papers to yellow and darken, but untreated papers either darkened more than treated papers or discolored the same.
discoloration from Bookkeeper® was not as strong as it was with Papersave®. The article was published in a newsletter with no anonymous peer review.


A conservation scientist at the Koninklijke Bibliotheek, Netherlands, provides a critical review of the literature including personal communications dealing with Papersave®, Battelle, Bookkeeper®, Libertec®, diethylzinc (DEZ), FMC-Lithco-MG3, Wei T'o®, Sablé, Separex®, and the Neschen (Bückeburg) deacidification/paper strengthening processes. Other paper strengthening processes (graft-copolymerization, paper splitting, and Vienna processes) are also discussed. The developmental histories, technical processes, treatment principles, advantages and disadvantages, and applications including health and safety, cost, and other considerations prior to 1996 are described in detail. A lengthy literature citation list and a list of contacts are provided. The article was published as a report with no anonymous peer review.


Conservation scientists at the Firestone Library, Princeton University, NJ (Stauderman) and the State University College at Buffalo, NY (Brückle and Bischoff) report results from testing the Bookkeeper® deacidification reagent on papers. A number of different types of papers were tested, and the results were evaluated using atomic absorption spectroscopy (AA), scanning electron microscopy/energy dispersive x-ray analysis (EDX/SEM), colorimetry, and pH. Replicate analyses showed that it was difficult, if not impossible, to apply sprays consistently. An airbrush provided the most uniform application. Magnesium oxide from Bookkeeper® did not penetrate from the sprayed side of the paper to the other side [suggesting that both sides of papers need to be sprayed to ensure effective deacidification]. Artificial thermal aging resulted in yellowing of the papers [consistent with alkaline darkening.] The article was published in conference proceedings with no anonymous peer review.

1995


The Preservation Projects Director of the Library of Congress reviews research findings in regard to large paper-based collections, photographic media, magnetic tape, and mass deacidification. A Swiss project found that naturally aged papers made until ~1950 had retained as much as 90% of their tensile strength but had lost 80% of their folding endurance. [This is typical of dry aging that causes an increase in the crystallinity of the cellulose, as opposed to humid aging (Williams and Krasow, 1973; Williams et al., 1977; Coffin et al., 2004; Tang and Jones, 1979; Caulfield and Gunderson, 1988; Daniels, 1989; Nissan and G. L. Batten, 1990; Padanyi, 1993; Brandis, 1994; Harris, 1995; Haermans et al., 1995; Moropoulou and Zervos, 2003; Karademir et al., 2004; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006).] A Norwegian study found that with an alkaline reserve, the presence of mechanical wood pulp did not negatively impact paper stability. Work at the Library of Congress involved developing and testing the diethylzinc (DEZ) mass deacidification process [no longer commercially available] and initiating a program to encourage and facilitate the development of other deacidification processes, particularly those that did not use Freon®. The article was published in conference proceedings with no anonymous peer review.

The Preservation Projects Director (Harris) and Preservation Research Officer (Shahani) at the Library of Congress describe the status of the Library's mass deacidification activities as of 1995. Akzo Chemicals withdrew their diethylzinc (DEZ) process from the market in April 1994. The Library then began an evaluation of the Preservation Technologies, L.P. (PTLP) Bookkeeper process, which uses micron (μm) size magnesium oxide particles and a surfactant suspended in a perfluorinated fluid to neutralize acids in paper (Leiner and Kifer, 1993; Leiner et al., 1998; Leiner et al., 2000; Kissa, 2001; Zumbühl and Wulfert, 2001; Järnberg and van Bavel, 2006; Guo et al., 2008). Plans for 1995-1997 were to work with PTLP to enhance the process, which would be followed by a demonstration project, and to encourage and evaluate other mass deacidification technologies. The article was published in a newsletter with no anonymous peer review.


A researcher at the TNO Centre for Paper and Board Research (The Netherlands) describes results from the European Project on the Effects of Pollutants on the Accelerated Ageing of paper (EU-STEP). Seven reference papers were specifically manufactured for the project, and three other naturally aged papers were used. The papers were deacidified using diethylzinc (DEZ), Sablé, and FMC-Lithco-MG3 processes, all of which left a slight odor on the papers. The alkaline reserve (AR) provided by the different processes was dependent on paper type. The Sablé process dissolved the paper sizing and/or the bookbinding glue; both Sablé and MG3 caused deterioration of inks; and DEZ produced "Newton-rings.” All processes produced papers with good mechanical performance, except thermal aging caused a slight decrease in the degree of polymerization of treated wood-free papers. DEZ and MG3, but not Sablé, decreased the rates of deterioration of wood-containing papers significantly so that the rates were comparable to those from wood-free papers. All processes protected paper from the effects of pollution. There are lists of conclusions and recommendations summarized from all the different project studies that were not described in detail in this article. The article was published in a journal with no anonymous peer review.


This PhD dissertation describes studies of paper degradation including effects of low-oxygen environments, sulfur dioxide (SO2) and nitrogen oxide (NO) acidic air pollutants, and the diethylzinc (DEZ) mass deacidification process. Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) did not provide enough reproducibility or sensitivity for studying cellulose and paper, but transmission FTIR did. Dry heat aging reduced the moisture content of the cellulose, but increased the aldehyde and ketone groups, which correlated with yellowing only for lignin-containing papers. Color change was not a universal method for evaluating paper degradation. Moist heat aging and acidic pollutant environments also reduced the moisture content, but cellulose deterioration did not occur until higher temperatures. Cellulose deteriorated less if aged in a low-oxygen environment. Decreased moisture content caused decreased folding endurance. The diethylzinc (DEZ) mass deacidification process provided a homogeneous alkaline reserve that protected the paper from acidic pollutants. The measured paper pH was not an effective indicator of paper protection, but the alkaline reserve was.


Researchers at the TNO Centre for Paper and Board Research (Havermans and Van Deventer) and the Dutch State Archives (Steemers) describe results from using gaseous diethylzinc (DEZ) to deacidify reference papers. A large number of tests were performed before and after artificial aging. Treatment produced a homogeneous deposition of zinc oxide (the source of alkaline reserve); thermal aging did not significantly impact the alkalinity of the treated papers, which remained between pH 7-8; and the deposited alkaline reserve (AR) was 1-2% calcium carbonate equivalent. Treatment did not decrease the tensile strength either with or without thermal aging, but the folding endurance after thermal aging...
was decreased for the treated paper. This was attributed to the predrying step of the treatment, which reduced the moisture content of the paper to less than 0.5%. Treatment helped to protect the paper from pollutant-induced degradation. There was no relationship between the pH of the treated paper and AR, and the AR was deemed the most important factor for protecting paper against acid attack. The article was published in a journal with no anonymous peer review.


A researcher at the Centre for Preservation and Conservation, German Library (Liers) and staff from Battelle (Schwerdt), the company that provides Papersave®, describe the first version of the Papersave® Battelle mass deacidification process. The process involved pre-drying books to a moisture content of ~ 1%, treatment, and post-drying, with the hexamethyldisiloxane solvent recycled. The drying steps involved microwave heating to 60 °C under vacuum, which had to be carefully regulated so that glow discharge did not occur. Covers that contained metal could not be treated. Ethanol was produced as a byproduct so that treated books had to be held in a separate room for two weeks prior to transferring them back into the stacks. The authors stated that the solvent had no negative effects on inks and dyes and left no odor [later results presented by Buisson (2004, 2006) showed the opposite]. The article was published in a journal with no anonymous peer review.


Conservation scientists at the National Library of the Netherlands summarize results from part of a study performed by the National Preservation Office of the Netherlands (CNC) to determine the impact of the Papersave® Battelle mass deacidification process on various library book materials. After treatment, the books had to be kept in a ventilated room for several weeks to reduce the odor that was left by the process, presumably residues of the hexamethyldisiloxane solvent and/or the ethanol byproduct used in the treatment. A number of tests were used to evaluate the process in relation to the materials including optical and olfactory observations; artificial heat and pollution aging; tests for lignin, pH, paper strength, and distribution of magnesium and titanium; and a statistical evaluation. An odor emanated from most books; there were Newton rings on some art papers; there was some bleeding of red and yellow inks; and the discoloration of treated papers varied after artificial heat aging. The process produced significantly lower folding and tear resistance in 41% of the papers before aging, but increased the folding and tear resistance after aging. The treatment was not homogeneous. The treatment positively affected books with rough paper, which was the only statistically significant trend. This summary of the report was published on the Koninklijke Bibliotheck web site.


The Chief and coworker at the Preservation Research and Testing Office, Library of Congress, report results from artificial aging of papers that had been doped with copper Cu(II) followed by deacidification. Immersion into aqueous solutions of bicarbonates extracted the Cu(II) ions from the paper, which reduced degradation. Spraying the aqueous bicarbonate solutions had no effect. Aqueous calcium hydroxide, magnesium acetate, calcium hydroxide followed by calcium bicarbonate, and non-aqueous methyl magnesium carbonate were ineffective at removing Cu(II). [The data suggest that non-aqueous and/or sprayed mass deacidification processes may have little impact on copper-catalyzed degradation of paper. The extraction of Cu(II) from the paper using bicarbonate solutions is reasonable because the stability constant for Cu(II) complexation by organic acid sites on the paper is smaller than for Cu(II) complexation by bicarbonate and carbonate, both of which are present in solution at the pH of the experiments.] The article was published as a report with no anonymous peer review.

A researcher at the Canadian Conservation Institute (CCI) summarizes results from the first portion of a five-part project to test diethylzinc (DEZ), Wei T'o®, and FMC-Lithco-MG3 mass deacidification processes on a number of different materials. The materials chosen for study were naturally aged papers (Phase I); new and artificially aged modern papers (Phase II); bindings, labels, media, and special papers (Phase III); papers damaged by pollution or bleaching (Phase IV); and proteinaceous materials such as leather bindings, parchment, animal glues, and photographs (Phase V). Results from Phases I-III have been published, and annotations of the final project reports can be found in this bibliography (Burgess and Kaminska, 1991; Burgess et al., 1992; Kaminska and Burgess, 1994). Phases IV and V have not yet commenced [perhaps because none of these processes are currently in use for mass deacidification]. Results from Phases I-III showed that all three processes damaged media, plastics, and book cover materials. A major problem was that Wei T'o® and FMC used organic solvents that dissolved organic materials (acrylics, organic colorants, wax seals, polystyrene envelopes, etc.). Pre-selection or testing was required for all processes to avoid damage. The summary of the reports was published on the CCI web site.


Scientists from 3M® Company provide an introduction to the general chemistry of perfluorocarbons (PFCs) and their use as substitutes for ozone-depleting substances (ODSs), which is relevant for evaluating the environmental impact of solvents used in the Bookkeeper® deacidification process. Since January 1, 1996, when the global manufacture of ODSs was terminated, PFC non-aqueous solvents have been increasingly used for special cleaning applications, particularly in the semiconductor industry. PFCs are virtually non-toxic, non-flammable, thermally and hydrolytically stable, and not ozone depleting. Detailed information regarding the physical properties of perfluorohexane (C₆F₁₄) and perfluoroheptane (C₇F₁₆) used in Bookkeeper® are given and compared to CFC-113 (C₂F₃Cl₃). Adding a high molecular weight fluorocarbon surfactant to the solvent increases the efficacy of removal of dirt particles [in analogy to the surfactant contained in Bookkeeper® that helps keep the magnesium oxide particles in suspension]. The inertness of PFCs and their long atmospheric lifetimes coupled with their high absorptivity in the infrared gives them a high global warming potential, but improvements in containment and recovery technology have reduced their emissions. The article was published in conference proceedings with no anonymous peer review.

1994


A preservation scientist at the National Library of Australia summarizes and evaluates test results from the response to the 1990 request for proposals issued by the Library of Congress to provide mass deacidification of books (Harris, 1990). The FMC-Lithco-MG3 process was deficient in the areas of alkaline reserve, completeness of deacidification, odor, and pH. The diethylzinc (DEZ) process dried the books, caused odor, and exposed the books to the highest temperatures (100 °C), but it left a higher alkaline reserve and gave more consistent deacidification than Wei T'o®. However, Wei T'o® resulted in better book condition, a higher moisture content, and less odor, but also exposed the books to a high temperature (80 °C). Human panelists who were used to detect odors from all treatments developed headaches and sore throats. All processes resulted in bleeding of dyes from the covers, texts, or illustrations; in yellowing or darkening of the paper; and in damaging the books so that they were distinguishable from untreated books. Folding endurance gave the best data for evaluating the physical stability of all papers tested in contrast to tensile strength, tensile stretch, and tensile energy
absorption. The Library rejected all three processes [none of which are currently commercially available for mass deacidification]. The article was published in a journal with no anonymous peer review.


Researchers from the University of Pittsburgh (Buchanan), the Carnegie Museum of Art (Bennett), Carnegie Mellon University (Domach, Tancin, and Whitmore), and Volute Preservation Management Associates (Melnick) evaluated the use of Bookkeeper® for the Library of Congress. The treatment extended paper lifetimes 2-4 times; the pH of most papers was raised from acidic to basic, but highly acidic books were not completely deacidified; the minimum 1.5% alkaline reserve (AR) standard was not always met; and the AR in the gutter areas was 30-50% of the AR elsewhere. There was no visible damage other than white residues and clamp marks on some covers, and colored inks on coated stock showed a slightly increased tendency to rub off. All the papers treated and heat-aged became more acidic, but at the same time, their AR increased, a phenomenon that was not explained. [The surfactant used to disperse the magnesium oxide particles is a polymeric perfluorocarboxylic acid that would be a stronger acid than acetic acid (pKa ~ 1.7), and 99% of it would remain in the paper after treatment (Leiner and Kifer, 1993; Leiner et al., 1998; Leiner et al., 2000; Kissa, 2001; Zumbühl and Wueffert, 2001; Järnberg and van Bavel, 2006; Guo et al., 2008).] Since 1994, the Bookkeeper® process has been improved to address all the deficiencies noted in this report. The article was published as a report with no anonymous peer review.


Researchers at the Centre de Recherches sur la Conservation des Documents Graphiques (CRCGD), Paris, France, describe the homogeneity of deposition of the alkaline reserve (AR) in the diethylzinc (DEZ), Wei T'o®, and FMC-Lithco-MG3 mass deacidification processes [none of which are currently commercially available for mass deacidification]. Atomic absorption spectrometry (AA) was used to quantitate zinc from the DEZ process and magnesium from the Wei T'o® and FMC processes at different locations on the surfaces of treated papers. Papers treated using Wei T'o® had an AR three times lower than those treated using FMC, but the distribution from the FMC process was heterogeneous. The DEZ process resulted in a high level of heterogeneity, a result of the heterogeneous moisture content in the papers. The article was published in conference proceedings with no anonymous peer review.


The Preservation Projects Director (Harris) and Preservation Research Officer (Shahani) at the Library of Congress describe work by Azco to improve the diethylzinc (DEZ) mass deacidification process. The objectives were to eliminate objectionable odors in treated books, minimize visual damage on book covers, and to evaluate the effect of the process on adhesives and all types of papers, inks, book covers, and other materials. The DEZ process was stated to be disastrous to photographic materials, and the odor and visual problems were not satisfactorily alleviated. Azco closed the DEZ plant in early 1994. The article was published as a report with no anonymous peer review.

Researchers at the Canadian Conservation Institute evaluated three mass deacidification processes that were in use at the time: diethylzinc (DEZ), Wei T'o®, and FMC-Lithco-MG3. Although none of these processes are currently used for mass deacidification, the experimental approach is noteworthy. The selection of sheets to test involved the same general approach as in Phase I of the project (Burgess and Kaminska, 1991) except modern papers were used. One set of duplicate non-control books was deacidified, whereas a second set was first artificially hydrothermally aged and then deacidified. Eight different chemical analytical plus empirical (appearance and odor) methods were used to evaluate the results. All methods negatively impacted book condition, but less so than for the naturally aged historic papers studied in Phase I. A significant difference between historic papers and new ones was that after aging, the moisture content dropped significantly for new treated and untreated papers. [This suggests that the cellulose in the historic papers was more crystalline (anhydrous) than the new papers.] New papers also profited more from deacidification than old papers. Deacidification resulted in a significant increase in the permanence of alum-rosin sized processed wood-pulp paper. Treatment of an already highly alkaline modern paper, however, resulted in its degradation. The article was published as a report with no anonymous peer review.


A researcher at La Route du Papier (Belgium) reports results from testing the mass deacidification processes available in 1990: Wei T'o®, Sablé, Bookkeeper®, diethylzinc (DEZ), FMC-Lithco-MG3, Book Preservation Associates (BPA), and the Vienna method. Test books were made from rag, chemical pulp, and mechanical wood papers, and a large number of writing inks were included. Parameters evaluated included paper and ink color changes, pH, alkaline reserve (AR) and distribution, degree of cellulose depolymerization, and copper number before and after artificial thermal and light aging. It was concluded that DEZ and Bookkeeper® were the best for all the papers, followed by Wei T'o®, FMC, and then Sablé. BPA was rejected. When it came to inks, DEZ and Bookkeeper® were again judged the best followed by Wei T'o® and FMC, then Sablé and BPA. The final order of preference given was: DEZ and Bookkeeper® were ranked higher than Wei T'o®, Sablé and FMC; and BPA and the Vienna methods were ranked as unacceptable. The article was published in a journal with no anonymous peer review.


Researchers at the National Library of the Netherlands studied the impact of the Papersave® Battelle and diethylzinc (DEZ) mass deacidification processes on volumes of bound newspapers and books that were treated and then artificially hydrothermally aged. Treatment with Papersave® caused some yellowing and resulted in an immediate worsening of paper strength in the majority of the samples. However, after artificial aging, the paper strength was higher than the untreated controls in most papers. Improvements in paper strength were correlated with lower quantities of lignin and higher initial paper strength, with no differences with respect to age or initial paper pH. DEZ resulted in all books having an odor, which lasted for more than a year after treatment; yellowing; Newton rings on most of the art paper; damaged synthetic bookbinding materials; and incomplete, inhomogeneous deacidification. The DEZ process also caused an immediate decrease in paper strength in the majority of papers. However, the trend reversed after artificial aging for more recent papers but remained the same or worsened for older papers. The trends were not, however, related to lignin, pH, or paper strength of the starting material. The article was published as a report with no anonymous peer review.


The Chief Conservation Officer of the Harry Ransom Humanities Research Center at the University of Texas at Austin describes the diethylzinc (DEZ) mass deacidification process [no longer commercially
available]. The gas-phase process involved five steps: (1) dehydration in an atmosphere of nitrogen, in which the moisture content of the paper was reduced to <1%; (2) permeation, in which DEZ was introduced into the chamber where it reacted with acids in the paper to form zinc compounds and with residual moisture in the paper to form the zinc oxide alkaline reserve; (3) inerting, in which excess DEZ was flushed from the chamber; (4) rehydrating, in which warm humidified air was introduced to rehydrate the paper; and (5) post-treatment, in which the odors were flushed from the papers. The process negatively affected plastics, adhesives, artists’ colors, book covers, photographs, and copying process papers. Polyester, cellulose acetate, cellophane, and thermofax papers were particularly damaged. Single-sheet items with a starting pH of 5-8 had a pH of 7.9-8.1 after treatment. Those with a starting pH <5 had a pH of 7.3-7.8 after treatment. The deposited alkaline reserve ranged from 0.5-1.2% zinc oxide. The article was published in a newsletter with no anonymous peer review.


Researchers at the Canadian Conservation Institute evaluated three mass deacidification processes that were in use at the time: diethylzinc (DEZ), Wei T’O®, and FMC-Lithco-MG3. Although none of these processes are currently used for mass deacidification, the experimental approach is noteworthy. A large number of prepared materials (different types of inks, pressure-sensitive tapes, plastics, glues, gums, book binding materials, etc.) including specifically bound books plus old donated materials such as postal stamps on envelopes, magazines and newspapers, architectural plans, color papers, vellum and parchment, photographs, works of art on paper, etc. were tested. Visual evaluation and color measurements were performed. All processes to some extent negatively impacted drawing inks, pencil crayons, watercolors, repair tapes, photographic papers, Mylar® book jackets, watercolors, cloth covers, plastic labels and pockets, cellulose acetate materials, and wax seals. Wei T’O® and FMC destroyed the images in color photocopies and laser copies. Tables give details of the damage for each item. The article was published as a report with no anonymous peer review.


Staff at Battelle (Germany) describes the original Papersave® Battelle process for mass deacidification. It is stated that the process solvent hexamethyldisiloxane is environmentally friendly and has low toxicity. [However, hexamethyldisiloxane is rated by European/International Regulations as being a R11 (highly flammable (explosive)) risk; a R50/53 risk (very toxic to aquatic organisms possibly causing long-term adverse effects in the aquatic environment); and it causes eye and skin irritation, may cause respiratory tract irritation, liver and kidney damage, blood effects, central nervous system depression, and tumors. No mention is made of negative impacts that include dissolving printing and writing inks and causing iridescence on illustrations, which was later noted by Buisson (Buisson 2004 and 2006).]

The article was published in a journal with no anonymous peer review.

1993


Researchers at the Staatliche Akademie der Bildenden Künste Stuttgart, Germany, (Banik), the Höhere Graphische Bundeslehr- und Versuchsanstalt, Austria, (Sobotka), and the Institut für Silikatchemie und Archäometrie, Austria, (Vendl and Norzsicska) report results from evaluating the effects of acidic pollutant gases, sulfur dioxide (SO₂) and nitrogen oxides (NOₓ), on modern book papers treated by using the diethylzinc (DEZ), FMC-Lithco-MG3, and Viennese (aqueous calcium Ca(II) hydroxide/methylcellulose) mass deacidification processes. All the papers were rosin-sized, and all except one acidic recycled paper had a neutral pH prior to treatment. All treatments resulted in the immediate reduction of paper strength (folding endurance). All treatments provided an alkaline reserve
except for the Viennese method that failed to provide an alkaline reserve for the acidic recycled paper. Treated papers absorbed more of the acidic gases than untreated papers [an expected result]. Although no data was provided, it was stated that there was evidence that the original rosin paper sizing was either removed or made ineffective by both the FMC and Viennese processes. The article was published in conference proceedings with no anonymous peer review.


This patent was to replace the Freon® solvent and surfactant in the original patent for the Bookkeeper® deacidification process. Although the patent states that magnesium oxide reacts with water to give magnesium hydroxide in a fast process, and deacidification reactions to neutralize acidity in paper require days, no data are provided to substantiate this. Instead of Freon®, perfluorocarbons (PFCs), perfluoromorpholine, and perfluoropolyoxymethers were proposed as solvents. The surfactant would be a perfluoropolyoxymethylen alkanolic acid for the perfluoropolyoxymethylen solvent; perfluoropolyoxymethylen alkanolic acid or potassium fluorooctanesulfonate (Forafac® 1033, a 50% aqueous solution of perfluoroocanesulfonic acid) or perfluoropolyoxymethylen alkanolic acid (Fomblin®) for the PFC solvent. In one example, the surfactant was present at 0.04% and the magnesium oxide at 0.15%. It is stated that the surfactant evaporates with the carrier. [However, 99% of the perfluoropolyoxymethylen alkanolic acid that is used with the PFC solvents remains in the paper.]


This third patent for the Bookkeeper® deacidification process describes treating a book by placing it in a V-shaped apparatus that fans out the pages as it is moved in a bath of the reagent. A dryer is included to heat-dry the books after treatment.


This report from the National Preservation Office of the Netherlands (CNC) describes data obtained from the 1990-1992 Mass Conservation Trial Programme. Conclusions were that millions of volumes were directly endangered, deterioration was continuing unabated, there was no single suitable method for mass conservation (including mass deacidification using diethylzinc (DEZ), Wei To®, FMC-Lithco-MG3, and Bookkeeper®), selection of materials for conservation should be focused on the period from 1840-1950, and environmental factors that impact paper degradation need to be studied. Recommendations were that major microfilming projects and commercial mass deacidification facilities for multiple users be created; preventive conservation (environmental control, air purification, better storage, etc.) be developed; and further research be conducted into the relationships between the causes and rates of deterioration of paper and into passive preservation methods. Another recommendation was that specific research be conducted into the preservation problems of audiovisual and electronic media. The four mass deacidification processes were evaluated by desk research, and a useful table is presented that shows their characteristic features as of 1993. The article was published as a report with some peer review.


A scientist at Amcor Research & Technology Centre, Victoria, Australia describes the physical aging of paper as a polymeric material, which is relevant for understanding how paper ages, the meaning of tensile strength tests, and natural and artificial heat aging (Williams and Krasow, 1973; Williams et al., 1977; Coffin et al., 2004; Tang and Jones, 1979; Caulfield and Gunderson, 1988; Daniels, 1989; Nissan
and G. L. Batten, 1990; Brandis, 1994; Harris, 1995; Havermans et al., 1995; Moropoulou and Zervos, 2003; Karademir et al., 2004; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006). The cellulose polymer contains both crystalline and amorphous regions, and physical aging occurs below its glass transition temperature (Tg), which for paper of 55% crystallinity is expected to be 55 °C for a normal moisture content of 7%; 23 °C for 12%; and -10 °C for 16%. During natural aging below the Tg, aging involves the slow relaxation of the glassy molecular network into the network free volume. As the free volume is reduced, the aging rate becomes increasingly slow, self-retarding. Aging causes an increase in the elastic modulii (an increase in stiffness/brittleness) and a decrease in stress relaxation rates. As cellulose is partially crystalline, changes in elastic modulii may not be measurable. Physical aging is reversed by heating above and then cooling below the Tg, or by adding moisture, both of which remove internal strains. Older papers absorb moisture more slowly. In viscoelastic mechanical testing of paper, the age of the paper is as important as temperature and relative humidity. Artificial heat aging is typically conducted at 60-100 °C at moisture contents such that the paper is aged near or above its Tg [implying that such artificial aging conditions may not reflect the natural aging of paper below its Tg]. The article was published in conference proceedings with no anonymous peer review.


This patent is for deacidification of books by placing sheets that contain calcium carbonate, bicarbonate, or other neutralization reagents in contact with acidic papers under pressure and humidity so that the acidic sheets are deacidified by migration of the neutralization reagents into the papers. The reagent in the deacidification sheet was present at a level of at least 0.1% by weight. The time required for migration decreased with increasing humidity and pressure. The same effect was found by dusting the paper with the alkaline solid, in which the time needed for neutralization was dependent on moisture content of the paper. The humidity was preferably at least 75%, and the pressure was preferably at least 0.1 psi. It was believed that migration of the neutralizing ions was facilitated by the formation of a continuous aqueous pathway from the condensation of water in small capillaries at the contact regions. It was also pointed out that an accurate evaluation of paper pH and acidity via static pH measurements and titrations, respectively, requires the addition of 0.1 M sodium chloride to ensure a high enough ionic strength and the migration of protons from inside the fibers' walls to the external solution.


Staff at the Battelle Institute, Germany, describes the Papersave® Battelle mass deacidification process. It used a non-aqueous liquid reagent that consists of magnesium titanium ethoxide in hexamethyldisiloxane, which was also stated to strengthen brittle paper by forming cross-links between hydroxyl groups of cellulose. Vacuum drying and microwave heating to 50-60 °C was first used to dehydrate the paper to a moisture content <1%. Then, the reagent was added to the chamber. After treatment, the solvent was removed, and the books were dried again. Original acidic paper pH values of 4.8-6.1 were increased to alkaline pH values of 8.8-9.1 by the treatment. The alkaline reserve was 1.2-2.2% magnesium carbonate depending on the starting pH of the paper. It was stated that previous undesirable side effects were considerably reduced. [Later work by Buisson (Buisson, 2006) showed that the process caused fading, solubilization of inks, iridescence on illustrations, and whitish deposits.] The article was published in conference proceedings with no anonymous peer review.


Researchers at the Department of Food Science and Technology, Tokyo University of Fisheries
(Tanaka, Huang, Ishizaki, and Taguchi) and National Pingtung Polytechnic Institute (Chiu) studied the reaction of chitosan, a linear polyamine, with glucose, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). The amine and glucose underwent the Maillard reaction so that, over time, a brown color developed and the concentration of free amino groups decreased. [The amino groups of aminoalkylalkoxysilanes can be expected to undergo Maillard reactions with carbohydrates and other components of paper (Kelly, 1979; Tanaka, 1993; Painter, 2001; Bosetto, 2002; De La Orden, 2002; Nursten, 2005; and Davidek, 2008).] The article was published in a journal with no anonymous peer review.


A conservator at the Bibliothèque Nationale (France) describes the use of the Sablé (virtually identical to Wei T'o®) process for deacidifying books on a mass scale. Books were placed on wire racks, dehydrated for 48 h at 60 °C in a vacuum autoclave to reduce the moisture content of the paper to less than 1%, then deacidified by immersion under pressure with methoxy-ethoxy methyl magnesium carbonate in a chlorofluorocarbon/alcohol solvent. The alcohol was then evaporated from the books for 12 h prior to packaging for shipment. Drawbacks included that hard covers of bound books bent because of the dehydration step; red or orange printing inks and pigments ran; some black-and-white illustrations showed iridescence; blue stamp inks ran; a strong smell of ethanol remained after treatment; parchment and leather bindings were not treatable; ink from paperback books from the later 20th century ran and the plastic layer on the covers was unstuck; the treatment did not provide a homogeneous pH or alkaline reserve (AR); and the AR after treatment only ranged from 0.2-0.9% calcium carbonate equivalent. No artificial aging tests were performed to address paper strengthening. The article was published in a journal with no anonymous peer review.


Staff at FMC Corporation Lithium Division describes physical testing results from using the FMC-Lithco-MG3 mass deacidification process after the solvent was changed from CFC-113 to heptane, and the deacidification reagent was changed to magnesium butyl glycolate. The article is primarily comprised of tables of data and graphs of the data to show that the process increased the strength of paper after artificial thermal aging. [It does not address other important issues that include bleeding of inks and other negative impacts that are discussed later in Brandis (1994).] The article was published in a journal with no anonymous peer review.

1992


An engineer at the Bibliothèque Nationale de France introduces the problem of paper acidity, the history of paper deacidification, and a description of mass deacidification processes available in 1992. [Although the Wei T'o®, diethylzinc (DEZ), and FMC-Lithco-MG3 processes are no longer commercially available for mass deacidification, their descriptions provide some general background to the science and technology of mass deacidification.] The Papersave® Battelle process was a variant of the Wei T'o® process. The Bookkeeper® process is still in use. The CSC Booksaver® process described is not the same as the current CSC Booksaver® process. Solvents, other ingredients, and the technology used in Papersave®, Bookkeeper®, and CSC Booksaver® have evolved and improved so comparative results from 1992 may not be currently applicable. The chlorofluorocarbon (CFC) solvents that deplete the ozone layer are no longer used in any current mass deacidification process in accord with the Montreal Protocol. The study was published as a book (English and French) with no anonymous peer review.

Researchers at the Canadian Conservation Institute evaluated three mass deacidification processes that were in use at the time: diethylzinc (DEZ), Wei T’o®, and FMC-Lithco-MG3. Although none of these processes are currently used for mass deacidification, the experimental approach is noteworthy. Four naturally aged books of different pulps and sizings were selected to provide sheets to be tested. Each book was unbound, its sheets were separated into four piles, and then each pile was rebound with buckram to give four identical sample books (16 total sample books). One book from each identical set of four was retained as untreated control, with the other three treated with DEZ, Wei T’o®, or FMC. Then, all 16 volumes were cut horizontally into two halves in which the top half was analyzed without further treatment and the bottom half was artificially hydrothermally aged. Books containing significant amounts of lignin were aged separately from the others. Eleven different chemical analytical plus empirical (appearance and odor) methods were used to evaluate the results. Odor was present for all processes, with DEZ being the worst and longest lasting. All treatments damaged the bindings. The most absorbent and thin paper was most susceptible to alkaline degradation. The article was published as a report with no anonymous peer review.


Researchers at the Centre de Recherches sur la Conservation des Documents Graphiques (CRCDG), Paris, France, describe results from artificial pollutant and hydrothermal aging of high-cellulose printing and newprint papers deacidified using ethyl magnesium carbonate in the Sablé mass deacidification process. The alkaline reserve (AR) of all treated papers was virtually unchanged after hydrothermal aging but decreased after pollutant aging with sulfur dioxide (SO₂) and nitrogen dioxide (NO₂). Neither type of aging caused depolymerization of cellulose in the printing papers, so their strength was unchanged. However, hydrothermal aging did cause more oxidation. Pollutant aging caused the treated printing papers to become more oxidized and brittle than untreated papers, whereas the strength of the newprint sheets remained relatively unchanged. [As both pollutant gases react with water to become sulfuric and nitric acids, respectively, it would be expected that the AR would decrease in pollutant-treated papers.] Why embrittlement occurred with the high-cellulose papers and not with the newprint papers was unanswered. [It may be related to the high levels of lignin and hemicelluloses in newprint that can serve as antioxidants and protective coatings for the cellulose.] The article was published in conference proceedings with no anonymous peer review.


Scientists in the Department of Chemistry and Materials Science Laboratory, Harvard University, studied the diethylzinc (DEZ) and FMC-Lithco-MG3 deacidification processes. Zinc from the DEZ process was present as zinc oxide (the alkaline reserve) throughout the surface and depth of uncoated paper. The FMC process resulted in bleeding of inks and a small deposition of magnesium oxide, but most of the FMC reagent was washed from the paper during the rinse cycle of the process before reactions could produce magnesium carbonate (the desired alkaline reserve). Neither method resulted in deacidification of glossy, coated paper. The article was published in a RSC (Royal Society of Chemistry) journal with anonymous peer review.


The Preservation Librarian at the Princeton University Libraries, New Jersey, describes results from
detailed evaluations of the impact of the diethylzinc (DEZ) and FMC-Lithco-MG3 mass deacidification processes on a large number of materials that might be found in or on books. [Although neither of these processes is currently in use, and they both negatively impacted most of the materials tested, the analysis is a good example of testing for chemical compatibility, an important factor when selecting a mass deacidification process.] Analyses included effects on covering materials, including binding adhesives, cloth, paper, illustration colors, and inks; whether or not paper cockled, discolored, or emanated an odor; whether hot-melt adhesives expanded or embrittled and cold-melt adhesives dissolved; whether call number labels or retrospective collections deteriorated during the process; and whether the treatment was complete and left an alkaline reserve. Before-and-after photographs are provided that demonstrate some of the negative effects. Tables are given that provide statistical data. The article was published in conference proceedings with no anonymous peer review.


An official of Akzo Chemical Company describes the development of the gas-phase diethylzinc (DEZ) mass deacidification process in collaboration with the Library of Congress. One main benefit was that it reacted instantaneously with carboxylic and other acids in paper to neutralize them, and with water to give zinc Zn(II) oxide and then Zn(II) hydroxide, which provided an alkaline reserve. Another significant benefit was that the final alkalinity from Zn(II) hydroxide was only pH 8.5, significantly less than the pH 10.5 from magnesium Mg(II) hydroxide or the pH 12.3 from calcium Ca(II) hydroxide, so that yellowing [alkaline darkening] and discoloration of pH-sensitive inks was minimal. However, there were disadvantages including odor and damage to books, with the main ones being that DEZ is pyrophoric, ignites spontaneously with the oxygen in air, and reacts explosively with traces of water. [The process is no longer commercially available]. The article was published in conference proceedings with no anonymous peer review.


Staff from Battelle (Germany) describes the first pilot plant and version of the Papersave® Battelle mass deacidification process. The Papersave® Battelle process was originally a modification of the Wei T'o® process that used methoxy magnesium methyl carbonate in a chlorofluorocarbon/alcohol solvent. Since then, the Papersave® process has been changed so that it now uses magnesium titanium alkoxide in hexamethyldisiloxane. The article was published in conference proceedings with no anonymous peer review.


Fifty participants, speakers, and observers from 27 institutions met to discuss management, selection criteria, funding strategies, toxicological, and other issues that would need to be addressed in relation to the emerging mass deacidification technology of 1992. The diethylzinc (DEZ), Wei T'o®, and FMC-Lithco-MG3 processes were the only commercial processes under consideration at the time. Several presentations describe results from comparative tests of the three processes. [None of these processes are currently commercially available]. The conference papers were published as a report with no anonymous peer review.

**1991**

Researchers at the Canadian Conservation Institute describe the project planning and selection of materials for a five-phase research project to evaluate diethylzinc (DEZ), Wei To®, and the FMC-Lithco-MG3 mass deacidification processes. [Although none of these processes are currently available for mass deacidification, the experimental approach is noteworthy. Annotation of the final project reports can be found in this bibliography (Burgess et al., 1992; Tse et al., 1994; Kaminska and Burgess, 1994) and a summary of the results at http://www.cci-icc.gc.ca/about-apropos/action/document-eng.aspx?Type_ID=8&Document_ID=126.] The article was published in conference proceedings with no anonymous peer review.


This patent is for simultaneous strengthening of deacidified paper by contacting the paper with hydrocarbon or halocarbon solutions of magnesium or zinc alkoxalkoxides that have been treated with carbon dioxide to have a low viscosity. The alkoxalkanols used included those exemplified by the trade names Cellosolves®, Carbitols®, and Carbowax®. The treatment resulted in a finish (coating) of the polymers on the paper to give a strengthening effect. Solvents used included Freon® and perchloroethylene.


A researcher at the Institut royal du Patrimoine Artistique, Belgium, summarizes textually and presents tables of findings from the literature and other sources regarding methods used for mass deacidification and strengthening paper through the year 1990. General descriptions of Wei To®, Archival Aids, Bookkeeper®, diethylzinc (DEZ), BPA, Vienna, FMC-Lithco-MG3, and parylene-N are given along with selection requirements, process details, and length of process. Results from each of the processes are summarized in regard to pH, uniformity of deacidification, alkaline reserve, mechanical resistance of the treated papers, odor, surface deposits, yellowing, and effects on inks and leather bindings. The total output of treated books per cycle, the cost per book, staffing needs, safety, and presence of chlorofluorocarbons (ozone depleters) are listed. Independent testing, advantages, disadvantages, and improvements suggested from the literature are included. The article was published in a journal with no anonymous peer review.


The product manager of FMC Corporation, producer of the FMC-Lithco-MG3 mass deacidification process, describes a recommended testing protocol for evaluating the impact of mass deacidification processes on paper. The testing would be conducted before and after artificial aging, and include tests of pH, alkaline reserve, brightness, yellowness, copper number, tensile strength tests, MIT folding endurance, and tear resistance. Also proposed is a metric to numerically categorize the extended and enhanced useful life (EEUL), which incorporates the impact before and after treatment with the impact before and after artificial aging on double hand folds. [Hand folds are highly uncontrollable, irreproducible, and subjective, so the rubric might be improved by substituting MIT folding endurance for the hand folds.] The article was published in a journal with no anonymous peer review.


Staff at FMC Corporation Lithium Division describes the use of a magnesium butoxytriglycolate polymer (MG-3) to simultaneously deacidify and strengthen paper. The process involved: (1) reducing the moisture content of the paper to 2% via dielectric heating; (2) immersing the books in a solution of MG-3; (3) draining the solution; (4) rinsing the books with fresh solvent; and (5) removing the solvent with dielectric heating. The process increased the strength, pH, and alkaline reserve of model papers after artificial aging. However, it decreased the brightness and increased the yellowness of the papers. [The article does not address other important issues that include bleeding of inks and other negative impacts that are later discussed by Brandis (1994).] The article was published in a journal with no anonymous peer review.

This bibliography by a librarian from the Preservation Directorate of the Library of Congress offers a broad presentation of the literature prior to 1990 related to mass deacidification. Citations include materials from scientific, library science, and popular works. The citations are arranged in chronological blocks, and an author index is included.

### 1990


Researchers at the Austrian National Library describe the use of the Viennese method for deacidification and strengthening of newspapers. Bound newspapers were unbound, immersed into an aqueous calcium hydroxide and methylcellulose solution, freeze-dried, and then rebound. Immersion in water caused the book block to swell extensively. [A later study indicated that the Viennese method failed to provide an alkaline reserve for acidic recycled paper, and there was evidence that the original rosin paper sizing was either removed or made ineffective by the Viennese process (Banik, 1993). Another later study concluded that the process was unacceptable (Liénardy, 1994).] The article was published in conference proceedings with no anonymous peer review.


Researchers at the Canadian Conservation Institute summarize a number of analytical methods that are used in studying effects of deacidification and artificial aging on paper stability. General descriptions of the methods for the analysis of paper, their benefits and disadvantages, are provided. Methods include determination of surface pH, cold extraction pH, iodometric intrinsic total acid, alkaline reserve, degree of polymerization, carbonyls, color measurements, and physical strength testing. The article was published in an AIC (American Institute for Conservation) journal with anonymous peer review.


This Request for Proposals, drafted by the Preservation Projects Director of the Library of Congress, describes the technical requirements for independent tests to be conducted on demonstration sets of papers treated by commercial mass deacidification processes during preliminary process evaluation (Harris, 2004). Tests included moisture content, odor evaluation, pH, alkaline reserve, leaching of inks and dyes, and completeness of deacidification. In addition, folding endurance, tensile strength, brightness, opacity, hot alkali solubility, and retention of alkaline reserve were to be tested after artificial hydrothermal aging. The article was published as a government report with no anonymous peer review.


The Preventive Conservation Manager of the National Archives of Canada describes the use of the Wei T'o® mass deacidification process for treating new paperbound and hardcover books, reports, and pamphlets. Books were vacuum dried at 60 °C to prevent the deacidification reagent from reacting with the moisture in the books; saturated with the deacidification solution that contained magnesium methyl
carbonate in a Freon®/alcohol solvent; and then vacuum dried. Some books could not be treated because of negative reactions with the alcohol-Freon® solvent. [The use of Freon® was discontinued in accord with the Montreal Protocol, and the process is no longer commercially available for mass deacidification.] The article was published in conference proceedings with no anonymous peer review.


Staff at Book Preservation Associates (BPA) describe the BPA mass deacidification process, which used the reaction between ammonia and ethylene oxide gas to form gaseous ethanolamine, which was the deacidification reagent. The process was harmful to leather, and the reagents are extremely toxic to humans. [The process is currently not commercially available]. The article was published in conference proceedings with no anonymous peer review.


This patent describes the use of monomers of either acrylates, methacrylates, acrylamides, methacrylamides, or nitriles to strengthen paper after in situ deacidification with an alkaline organometallic compound (metal alkyl, metal alkoxide, or alkyl metal alkoxide). The deacidified paper (wet with the treatment solvent such as Freon®) was treated with a monomer and then vacuum and heat-dried to polymerize the monomer to give a polymeric coating that strengthened the paper.


Staff from Preservation Technologies, L.P. describe the history and approach behind the Bookkeeper® mass deacidification process. At the time, Freon® was used as the solvent for the magnesium oxide particles and surfactant. Freon®, an ozone-depleting substance, was later changed to perfluoroheptane in response to the Montreal Protocol. [As virtually all of the surfactant, which serves to keep the magnesium oxide dispersed in the perfluoroheptane solvent, is absorbed on the paper, the mechanism for retention of the particles on the paper is not clear.] The humidity used in artificial aging tests had a significant impact on the folding endurance of treated vs. untreated papers. Using dry heat, aging significantly decreased the folding endurance of both treated and untreated papers. Using humid heat, aging decreased the folding endurance of both treated and untreated papers, but the strength of untreated papers decreased more than the strength of treated papers. The article was published in conference proceedings with no anonymous peer review.


Researchers at the Institut Royal du Patrimoine Artistique (Belgium) review, make recommendations, and provide working methods for a large number of aqueous and nonaqueous deacidification treatments in use in 1990. They describe the impact of the treatments on pH; alkaline reserve; paper strength; brightness; iron gall, writing, marking, and ballpoint inks; pastels and water-colors; and health and safety and other practical concerns. Bar graphs show that aqueous treatments with 0.01 M calcium Ca(II) hydroxide and 0.04 M magnesium Mg(II) bicarbonate both gave improved folding endurance, improved brightness, and improved alkaline reserve compared to untreated paper after humid artificial aging. The pH of papers treated with Mg(II) bicarbonate was significantly higher than those treated with Ca(II) hydroxide, particularly for rag paper after humid aging. It was stated that dry aging of Mg(II) bicarbonate treated papers resulted in negative results. [However, none of the aging conditions nor other experimental details were given, and none of the actual numerical data were provided so the data are difficult to evaluate.] The article was published in a journal with no anonymous peer review.

The editor of a conservation newsletter presents an editorial point of view regarding decision-making for librarians in terms of mass deacidification and microfilming. Factors suggested include: (1) cost; (2) obsolescence of a book vs. its enduring value, in which books are maintained for a period of time without either type of preservation to determine which should be microfilmed to preserve its apparent enduring value, thus eliminating the need for deacidification; (3) the usefulness of the format for scholars and students, in which microfilm is generally less used and/or desired; (4) the relative value of an original vs. a copy, in which the copy does not contain crucial information that may be needed for some books and some researchers; (5) security, in which the chance of loss, deterioration, or destruction of a microfilm master before the passage of 500 years may need to be considered; and (6) practicality of monitoring in a national database the preservation actions taken by various libraries. A conclusion was that if a given book were acidic but strong, and of likely enduring value, it would be a candidate for deacidification. Conversely, if a book were brittle and likely to be of enduring value, it would be a candidate for microfilming. The article was published in a newsletter with no anonymous peer review.


A Preservation Officer at the University of Tulsa describes the dedication event on May 7, 1990, for the FMC Corporation's paper preservation plant in Bessemer City, North Carolina. The demonstration plant had a capacity for deacidifying and strengthening 300,000 books per year. Plans were to construct four operating plants with operating capacities of 1-4 million books per year. [The process is no longer commercially available.] The article was published in a newsletter with no anonymous peer review.


A consultant (Nissan) and the manager of research and development at Georgia-Pacific Corp., Decatur, GA (Batten) describe the contribution of hydrogen bonding to the tensile strength of paper, which is relevant for understanding the impact of degradation and deacidification on paper (Williams and Krasow, 1973; Williams et al., 1977; Coffin et al., 2004; Tang and Jones, 1979; Caulfield and Gunderson, 1988; Daniels, 1989; Padanyi, 1993; Brandis, 1994; Harris, 1995; Havermans et al., 1995; Moropoulou and Zervos, 2003; Karademir et al., 2004; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006). Paper stiffness is described by the Young's (elastic) modulus, which is the slope of the beginning elastic portion of the xy-plot of strain (stretch) vs. stress (force) when paper is stretched to its breaking point. In the elastic region, release of the stress will return the paper to its original length. A high modulus describes stiff paper that resists deformation under longitudinal stress and has high tensile strength, such as old brittle paper that breaks under a high load while still in the elastic region. A low modulus describes more flexible paper of lower tensile strength that stretches and eventually breaks under a lighter load in the inelastic plastic region of the curve, such as old paper made more flexible by conservation treatments. This is why the tensile strength of aged paper may be high but the folding endurance low: Brittle paper does not stretch, but it does easily break with folding. The Young's modulus is directly related to the density of the hydrogen bonds within and between the cellulose fibers so that the modulus primarily reflects interfiber bonding. All hydroxyl groups in paper participate in hydrogen bonding, so their removal by oxidation reduces elasticity and tensile strength. The article was published in a journal with anonymous peer review.


A researcher at the Tokyo University of Agriculture and Technology, Japan, describes deacidification of acidic wood-free paper using the Wei T'o® and diethylzinc (DEZ) mass deacidification processes. Wei
T'o® was more effective than DEZ for increasing the folding endurance after artificial hydrothermal aging. The DEZ process was further studied, however, because it did not dissolve dyes or plastics. Neither process was as effective on aged paper as compared to unaged paper. The residual moisture content in the paper had to be significantly reduced so that the DEZ did not simply react with the water and form an impervious layer of zinc hydroxide that would prevent penetration of the gaseous DEZ into the paper fibers. The article was published in conference proceedings with no anonymous peer review.


A researcher at the Library of Congress (Sebera) and a preservation consultant (Sparks) describe the status of the Library’s diethylzinc (DEZ) mass deacidification process as of 1990. The process had advantages and disadvantages, and data from its use have been reviewed elsewhere in this annotated bibliography (Oberholzer, 2006; Porck, 1996; Havermans, 1995; Brandis, 1994; Liénardy, 1994; Havermans, J., R. Van Deventer, and T. Steemers, 1995; Burgess, 1992; Stroud, 1994; Harris, 1994; Pauk, 1994). [The process is no longer commercially available]. The article was published in conference proceedings with no anonymous peer review.


The inventor of the Wei T'o® mass deacidification process describes the state-of-the-art in mass deacidification as of 1990 and introduces the history and chemistry of acid hydrolysis and deacidification of paper. One informative discussion is that it is not sulfuric acid "as is generally stated in library literature" that accounts for the acidity of paper. It is the hydrolysis of the hydrated aluminum Al(III) ion from papermakers alum, and the organic acids formed during paper degradation, that result in an acidic paper pH, which is usually pH 4-5. [It has been known for many years that the hydrated Al(III) ion and the organic acids are all weak acids with comparable pKa values of ~ 4-5 (Akitt, 1972).] The mass deacidification processes of the time, diethylzinc (DEZ), Wei To®, Bookkeeper®, and methods using amines, were summarized. [Of the processes described, Bookkeeper® is the only one currently commercially available for mass deacidification]. The article was published in conference proceedings with no anonymous peer review.


A preservation consultant presents factors that need to be considered when selecting a mass deacidification process. It is stated that deacidification does not preserve already brittle paper, but it helps stronger paper remain strong longer. The high production capability of mass deacidification provided an economy of scale and a relatively short time for deacidification of large collections. The lifetime of paper that contained an alkaline reserve (AR) of 1-2% might have been increased by 3-5 times. The 10-year lifetime of cheap groundwood paper could be extended to 30-50 years. The 100-year lifetime of a stronger paper could be extended to 300-500 years. Perhaps the most important consideration in selecting a process was to minimize unwanted side effects on inks, dyes, adhesives, bindings, and other non-paper materials. A number of other specifications are given that include the effectiveness of the process, uniformity of AR, quality assurance, process engineering, toxicity and other health hazards during process engineering and with handling final deacidified materials, environmental impact, costs, and security. The article was published as a report with no anonymous peer review.

1989


A researcher in the Department of Conservation at The British Museum presents a non-technical
introductory review of issues related to oxidation of paper. It is stated that cellulose undergoes oxidation to give aldehyde and/or ketone carbonyl groups that can cause yellowing. Worse is that oxidation causes chain scission, which results in loss of tensile strength, and cross linking, which results in brittleness but an increase in tensile strength. Oxidation was particularly relevant for papers that contained lignin because it was thought that the lignin phenolic groups formed free radicals that were transformed into colored products that caused yellowing. However, dark aging of lignin-containing papers also resulted in yellowing. Strongly alkaline conditions increased the rate of oxidation; and transition metal ions such as iron and copper accelerated free-radical oxidation reactions. Zinc oxide in UV light catalyzed the formation and decomposition of peroxides to give free radical oxidizing agents. Magnesium Mg(II) compounds protected cellulose from oxidation during alkaline oxygen bleaching of pulp by removing transition metals that catalyzed the decomposition of peroxides. Artifacts may be harmed by storage in cardboard, wood, and other oxidizable materials because of the evolution of peroxides. Lignin, xylan, and other carbohydrates can be oxidized to produce peroxides that can then initiate the decomposition of cellulose. The article was published in conference proceedings with no anonymous peer review.


A researcher at the Zentrum für Bucherhaltung in Leipzig, Germany, in conjunction with IFLA and UNESCO, provides an excellent introduction to issues involved with preservation of library materials. Damages are categorized as (1) physical-mechanical, (2) biological, and (3) chemical, and examples of each are given. The structure, decomposition, and decomposition products of cellulose, and impact of refining, are presented in a pedagogical manner. Statistics show that the situations of libraries and archives of the time were not particularly conducive to preservation of highly endangered acidic, wood pulp paper. The diethylzinc (DEZ), Wei T'o®, and other mass deacidification processes of the time are described. Methods of restoration of brittle paper included leaf casting, which fills holes in paper with paper fibers; paper splitting, in which the paper is split longitudinally and the core is stabilized; and lamination, which melts a synthetic plastic sheet into the paper. As lamination is virtually irreversible, encapsulation between two sheets of polyethylene terephthalate is preferred. The article was published as a report with no anonymous peer review.


Scientists at the Central Research Laboratory, Oji Paper Company, Tokyo, Japan describe the use of simulations to depict the irreversible dimensional responses of paper during cyclic humidity changes, which is relevant for the storage of paper. During slow cycles (one day for the half cycle), the simulations showed that paper irreversibly expanded or shrunk according to the moisture change (expanded with moisture, shrunk with drying). The first exposure to higher humidity and the subsequent drying resulted in a significant irreversible shrinkage, but the dimensional response in the range of low humidity was substantially reversible. The same was observed for paper curling, which was caused by differential structural variation in the sheet. The article was published in a Springer journal with anonymous peer review.

**1988**

A research chemist (Caulfield) and a research general engineer (Gunderson) at the USDA Forest Service, Forest Products Laboratory, Madison, WI, describe strength properties of paper, which is relevant for understanding paper stability (Williams and Krasow, 1973; Williams et al., 1977; Coffin et al., 2004; Tang and Jones, 1979; Daniels, 1989; Nissan and Batten, 1990; Padanyi, 1993; Brandis, 1994; Harris, 1995; Havermans et al., 1995; Moropoulou and Zervos, 2003; Karademir et al., 2004; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006). Tensile strength (TS) primarily reflects interfiber bonding by measuring the force needed to stretch paper to its breaking point. Brittle, inelastic paper that contains more crystalline cellulose and less water has high TS because bonds are not easily stretched along crystallographic planes. More pliable, stretchy, viscoelastic paper has low TS because it contains cellulose that is more amorphous and more hydrated. Zero span breaking length reflects individual fiber strength. Tearing resistance primarily reflects interfiber bonding by measuring the work needed to tear a piece of paper. More work is needed to break interfiber bonding than to break a fiber, so papers made from longer fibers have greater tearing resistance. However, as interfiber bonding increases, fibers become more likely to break than to separate, so papers made using enhanced fiber-bonding processes such as beating have decreased tearing resistance. Folding endurance measures the overall viscoelastic properties of paper because it is the ability of the paper to maintain strength after repeated folding under tension. Poor folding endurance can result from short fibers, poor interfiber bonding, or too much interfiber bonding that leads to brittleness. Preconditioning at 22-40 °C and 10-35% relative humidity (RH) followed by conditioning at 23 °C and 50% RH is vital for obtaining repeatable test results. A rag bond paper is shown to have TS and tearing resistance intermediate between offset and newsprint papers, but a folding endurance 1-2 orders of magnitude greater than more brittle papers. The article was published in conference proceedings with no anonymous peer review.


This report by the Office of Technology Assessment of the US Congress provides a useful overview of different mass deacidification processes (Wei T'o®, diethylzinc (DEZ), Bookkeeper®, and interleap vapor phase deacidification (VPD)) that were available for use by the Library of Congress in 1988. At the time, the Library was actively involved in developing the DEZ process, so much of the report describes the process, effectiveness, costs, safety, and health and environmental effects of DEZ. A chapter describes the above three alternatives to DEZ, their advantages and disadvantages including the need for preselection and predrying; cycle time; complexity of treatment plant; effect on inks, colors, plastic book covers, and other materials; completeness of neutralization, pH, and alkaline reserve after treatment; impacts on health and environment; stage of development; and cost. At the time, Freon® was used in both Wei T'o® and Bookkeeper®, but was later changed to another solvent in accord with the Montreal Protocol. Other processes that were in some use were briefly described, including Sablé, Kathpalia, Neschen (Bückeburg), and Graft-copolymerization. The status of alkaline paper production, its advantages and disadvantages to manufacturers, were discussed. The article was published as a report with peer review.

**1987**


A researcher at the Library of Congress summarizes two gas-phase mass deacidification processes available in 1987 based on morpholine or diethylzinc (DEZ). The morpholine process did not leave a permanent alkaline reserve (AR), and the DEZ process caused Newton rings on book covers and was explosively reactive with oxygen in air. The article was published in a monograph with no anonymous peer review.
1984


Researchers in the Department of Chemistry, Texas A&M University, used Langmuir adsorption isotherms to evaluate the adsorption of butyl amine and pyridine on Florisil®, an amorphous magnesium silicate that contains acid sites, which is background chemistry for the proposed use of aminalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). The isotherms were interpreted using the "patch theory" of adsorption that suggests that at low-coverages, the amines were chemisorbed onto acid sites and that at higher coverage, they were physisorbed [chemisorption possibly occurring with adsorption of aminalkylalkoxysilanes onto acid sites in paper]. The plotted adsorption isotherms provide insight into the physical meaning of the isotherm shown in Cheradame (2004). The article was published in an Elsevier journal with anonymous peer review.


This is the first patent for the Bookkeeper® mass deacidification process. The process involved using micron (μm) size particles of a basic metal oxide, hydroxide, or salt dispersed in a gas or liquid halogenated hydrocarbon with a surfactant. The halogenated hydrocarbon was Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and the surfactant was Fluorad® FC 740, a nonionic fluorinated alkyl ester made by 3M® Company. An example was given of a tank deacidification in which magnesium oxide was at a concentration of 0.02% and the surfactant was at a concentration of 0.01%. According to the Material Safety Data Sheet (MSDS) for Fluorad® FC 740, it contains 45-50% of the heavy aromatic solvent petroleum naphtha (CAS no. 64742-94-5), 50% fluoroaliphatic polymeric esters (proprietary), 1-5% naphthalene, and < 2% residual organic fluorochemicals. The naphtha solvent contained a large quantity of C10-C12 alkyl benzenes. The molecular weight and vapor pressure of the fluoroaliphatic polymeric ester surfactant was not given.


A statistician conducted a condition survey of 1200 books from the General and Law Collections of the Library of Congress to obtain an estimate of the percentage of all Library books that would benefit from mass deacidification. Items excluded from the survey included rare books, manuscripts, microfiche, and directories. Information on paper strength (MIT folding endurance), acidity (pH), lignin content, age, binding condition, and call number were included in the survey. No results are contained in the report, but graphs of pH vs. percentage of books, and pH vs. age, can be found in Shahani et al. (2000). The article was published as a report with no anonymous peer review.

1982


Scientists at the Conservation Center of the Institute of Fine Arts, New York University (Nelson); Museum of Modern Art (King); Department of Chemistry, Brooklyn College, City University of New York (Indictor); and the Department of Chemistry, Brookhaven National Laboratory, Upton (Cabelli), New York, describe effects of soaking/washing paper in different types of water (distilled, deionized, and tap) on the mechanical strength of more permanent papers, which is relevant for understanding the impact of aqueous deacidification processes, such as the Neschen (Bückeburg) process, on paper (Tang and Jones, 1979; Tang, 1981; Moropoulou and Zervos, 2003). After artificial dry oven aging of the papers, use of tap water did not negatively impact the folding endurance of Whatman and newsprint papers, but
use of deionized and distilled water did. Use of tap and deionized water did not negatively impact an alkaline paper that contained 3% calcium Ca(II) carbonate, but distilled water did. Neither tap nor the highly purified waters were recommended for conservation use. [This is why modern conservators, as per the advice in the Paper Conservation Catalog, 7th Edition, 1990, http://cool.conservation-us.org/coolaic/sg/bpg/pcc/16_washing.pdf, avoid washing paper in deionized water.] The article was published in an AIC (American Institute for Conservation) journal with anonymous peer review.

1981


This PhD dissertation describes results from studying the impact of cobalt Co(II) on the alkaline oxidation of a model cellulose compound, which is relevant for understanding the impact of transition metal ions and deacidification reagents on the oxidative stability of paper. In an alkaline oxidative system, peeling reactions, stepwise elimination of monomers from the reducing end of the cellulose chain, are stated to be less important than depolymerization reactions or reactions that cleave carbohydrate rings. These reactions are generally initiated by oxidation of cellulose hydroxyl groups to carboxyls via hydroxyl free radicals formed from peroxides. Formation of the hydroxyl radicals from peroxides is catalyzed by transition metal ions. However, coordination of Co(II) to cellulose hydroxyl groups and a catalytic oxidation-reduction cycle between Co(II) and Co(III) also contribute to oxidative degradation. [This mechanism may also explain oxidation of paper by iron gall ink.] Formation of adsorptive precipitates at alkaline pH, such as insoluble hydroxides, removes metal ions from solution, making them unavailable for catalysis [analogous to how magnesium Mg(II) salts at alkaline pH inhibit oxidation reactions (Corbett, 1973; Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Strlić et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008)]. Silicate anions, however, common in pulp and paper, enhance oxidation rates by solubilizing metal ions and promoting oxidation-reduction cycles. To prevent this enhancement, it is important to first form the metal hydroxide precipitant first, or deacidify first, before adding a complexing reagent.


A scientist in the Preservation Office, Library of Congress, describes the use of distilled or deionized water that contains calcium Ca(II) hydroxide to simultaneously wash and deacidify paper, which is relevant for understanding the impact of aqueous deacidification processes, such as the Neschen (Bückeburg) process, on paper (Tang and Jones, 1979; Nelson et al., 1982; Moropoulou and Zervos, 2003). An interesting finding was that the amount of Ca(II) that was absorbed by both newsprint and Kraft paper reached an upper limit when the solution concentration of Ca(II) was ~36 mg L⁻¹, but the newsprint paper absorbed approximately twice as much Ca(II) (9700 mg per kg paper) than the Kraft paper (4840 mg per kg paper). [These data indicate that the newsprint had approximately twice as many adsorptive active sites than the Kraft paper, which could be caused by the presence of lignin and/or other complexing components in the newsprint.] After dry and moist artificial heat aging, folding endurance of papers treated with Ca(II) increased significantly over untreated papers. As the Ca(II) was provided as the hydroxide, the paper pH was also made alkaline, and the treatment left an alkaline reserve. These results contrasted with using pure distilled or deionized water, which significantly negatively impacted the stability of paper. The article was published in conference proceedings with no anonymous peer review.

A researcher at the Library of Congress describes the requirements for mass deacidification and discusses processes including the use of amines, which is relevant for the use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). Requirements included that the paper must be uniformly neutralized, buffered as close to pH 7 on the alkaline side to prevent yellowing [alkaline darkening], and contain an alkaline reserve (AR) of 3% calcium carbonate equivalent after treatment for maximum permanence. The reagent must not leave an odor, the treated paper must be non-toxic, no new problems can be introduced, the life of the paper must be significantly extended, and the treatment must be reasonable in cost. The use of amines as deacidification reagents was not acceptable because amines can seriously discolor paper via the Maillard reaction (Tanaka, 1993; Painter, 2001; Bosetto, 2002; De La Orden, 2002; Nursten, 2005; and Davidek, 2008). Further, fixing an amine via polymerization or reaction with the cellulose did not provide improved aging characteristics and seriously discolored the paper [which would also be expected for the use of aminoalkylalkoxysilanes as deacidification reagents]. The conclusion was that amines offer little hope of permanent deacidification while seriously damaging the paper. The article was published in conference proceedings with no anonymous peer review.


Scientists in the Preservation Office of the Library of Congress describe effects of soaking/washing paper in different types of water, including distilled, deionized, tap, and deionized water passed through a column of calcium Ca(II) carbonate chips, on the mechanical strength of paper, which is relevant for understanding the impact of aqueous deacidification processes, such as the Neschen (Bückeburg) process, on paper (Tang, 1981; Nelson et al., 1982; Moropoulou and Zervos, 2003). Washing with ultrapure water (distilled or deionized) that contained no calcium Ca(II) had a deleterious effect on paper strength after artificial aging in dry and humid ovens. Washing with tap water was better, but it was discouraged because tap water contains chlorine and transition metal ions that can contribute to paper oxidation. Washing with distilled or deionized water that was passed through a calcium Ca(II) carbonate column, however, did not shorten the life of the paper. [The deleterious effect on paper strength of soaking/washing paper in deionized water is why modern conservators, as per the advice in the Paper Conservation Catalog, 7th Edition, 1990, [http://cool.conservation-us.org/coolaic/sq/bpg/pc/16_washing.pdf](http://cool.conservation-us.org/coolaic/sq/bpg/pc/16_washing.pdf), avoid washing paper in deionized water.] The article was published in an AIC (American Institute for Conservation) journal with anonymous peer review.

1977


This patent describes the use of aminopropyltrimethoxysilane and other silanes as hair setting agents that leave a layer of film-forming material on the hair, an application that is similar to the proposed use of aminoalkylalkoxysilanes as paper deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). The formulations provide a hard, flexible, and shiny coating on the hair that is partially retained even after shampooing. [This suggests that treatments using aminoalkylalkoxysilanes polymerized on paper may not be easily reversible.]

Scientists in the Preservation Research and Testing Office of the Library of Congress provide a literature review and results from artificial aging of paper deacidified using sodium Na(I), calcium Ca(II), and magnesium Mg(II) carbonates in the presence of catalytic (ppm) amounts of copper Cu(II), which is relevant for understanding the impact of mass deacidification reagents on the oxidation of paper. Alkalizing paper to a pH of 10 with Na(I) carbonate caused paper to darken, oxidize, and degrade, with the effects more pronounced for humid-oven as opposed to dry-oven aging. Ca(II) and Mg(II) carbonates did not cause such pronounced negative effects. Transition metal ions accelerated oxidation and embrittlement of paper during humid-oven aging, but not during dry-oven aging. Naturally aged brittle papers retained their tensile strength suggesting that fiber-to-fiber bonds remained strong perhaps from increased crystallinity of the cellulose. However, the brittle papers lost their folding endurance because the fibers themselves degraded, perhaps because during the aging process, the originally moisture-rich amorphous regions of the fibers had been depolymerized or "cut" by hydrolysis, then became crystalline and lost their plasticizing water, and consequently became brittle. Mg(II) carbonate at alkaline pH protected paper against transition metal ion catalyzed oxidation, but Ca(II) carbonate did not (Corbett, 1973; Sinký, 1973; Corbett and Thompson, 1973; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Strlič et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). Iodides protected paper by eliminating peroxides. It was stated that using the Arrhenius equation to predict paper life needed to take into account all variables, including temperature, humidity (moisture content of the paper), pH, alkaline reserve, and the presence of oxidation catalysts. The article was published in conference proceedings with no anonymous peer review.

1976


A scientist in the Division of Biological Sciences, National Research Council of Canada, Ottawa, describes how ultrasound energy during sonication breaks down microfibrils (strands) of cotton cellulose in water into their elementary fibrils ("fibrillation") (Prozorov et al., 2004; Kolpak and Blackwell, 1975). This is related to the Kundrot patent (Kundrot, 1999) that uses sonication of metal oxide particles in a gas-solid fluidized bed to deacidify papers and books. Sonication in a gas-solid fluidized bed may not break down the cellulose in paper as does aqueous sonication, but the impact of sonication from a gas-solid fluidized bed on cellulose in paper has not been reported. The article was published in a Wiley journal with anonymous peer review.

1975


Scientists in the Department of Macromolecular Science, Case Western Reserve University, OH describe how sonication of microfibrils of cotton cellulose in water results in their breakdown into elementary fibrils ("fibrillation") (Prozorov et al., 2004; Colvin, 1976). This is related to the Kundrot patent (Kundrot, 1999) that uses sonication of metal oxide particles in a gas-solid fluidized bed to deacidify papers and books. Sonication in a gas-solid fluidized bed may not break down the cellulose in paper as does aqueous sonication, but the impact of sonication from a gas-solid fluidized bed on cellulose in paper has not been reported. The article was published in a SAGE journal with anonymous peer review.

1973

This report from researchers at The Institute of Paper Chemistry, Appleton, Wisconsin, describes results from alkaline (pH 14) oxygen bleaching of pulp at 100 °C, which is relevant to understanding the impact of alkaline deacidification reagents on paper oxidation (Sinky, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Strič et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). Trace levels of transition metal ions catalyzed decomposition of peroxides into free radicals, which degraded cellulose. Magnesium Mg(II) salts inhibited the oxidation. It was suggested that Mg(II) "oxo" or "hydroxo" compounds dissolved and then penetrated the fiber wall to form coordination compounds with the transition metal ions to prevent electron transfer reactions. High-cellulose pulps were more inert toward oxidation than lignin-containing pulps. Most degradation occurred in the first 15 min, and the greatest carbohydrate degradation occurred for pulps with the highest lignin because lignin was thought to be oxidized into peroxides in which oxidation products were carbonic acid and organic acids. Artificial heat aging at 105 °C resulted in pyrolytic decomposition of more stable organic peroxides into hydrogen peroxide, which caused additional bleaching and degradation. It was not known whether this would occur upon natural aging, however. Before bleaching, extraction of the pulp with alkali removed oxygen-consuming material. Reduction with borohydride reduced the rate of consumption of oxygen but not the total oxygen consumed, indicating that the presence of the reducing agent slowed down the oxidation but did not inhibit it. The article was published as a report with no anonymous peer review.


This report from researchers at The Institute of Paper Chemistry, Appleton, Wisconsin, describes results from alkaline (pH 14) oxygen bleaching of pulp, which is relevant to understanding the impact of alkaline deacidification reagents on paper oxidation. Oxidation reactions were immediate, and the source of the free radical initiators leading to peroxide formation was lignin. Subsequent reactions of the peroxide lead to polysaccharide (cellulose) degradation and loss of fiber strength. Higher alkalinity resulted in greater oxidation of lignin phenols and carbohydrate hydroxyl groups because they deprotonated to give phenolates and alcoholates, respectively. There were physical and chemical changes in fibers with alkali and heat. Alkali decreased the softening temperature of lignin and hemicellulose, causing the pulp to become plasticized (lignin flowed on the surface of fibers at high, 120 °C, temperatures). Upon cooling, it was suggested that the plasticized components solidified and "spot welded" neighboring fibrils. The chemical reactivity of lignin also changed due to plasticization and chemical condensation of the lignin fragments. These physicochemical factors were suggested to result in cross-linking, stiffness (brittleness), and weakening of the fibers. However, oxygen and alkali together appeared to weaken the "spot-weld" cross-links to increase fiber flexibility. The article was published as a report with no anonymous peer review.


This PhD dissertation by a student at the Institute of Paper Chemistry at Lawrence University, Appleton, Wisconsin, describes effects of magnesium Mg(II) salts on the transition-metal catalyzed degradation of a cellulose model during alkaline oxidation, which is relevant for understanding the impact of Mg(II)-containing deacidification reagents on paper oxidation (Corbett, 1973; Corbett and Thompson, 1973; Williams et al., 1977; Graves, 1981; Liénardy and van Damme, 1990; Glusker et al., 1999; Gavriliu et al., 2001; Malesic et al., 2001; Mordasini et al., 2003; Strič et al., 2004a, 2004c, 2004d; Baty and Sinnott, 2004; Wójciak, 2006; Logenius et al., 2008). High-temperature (120 °C) oxidation first caused...
formation of peroxides in which hydrogen peroxide, as opposed to organic peroxides, was the main peroxide formed. Then, transition metal ions catalyzed the decomposition of the hydrogen peroxide to give the final oxidizing agents, hydroxyl and perhydroxyl free radicals. Mg(II) salts, which in alkaline water become Mg(II) hydroxides, inhibited oxidation of the cellulose by "deactivating" the transition metal ions so that they could not catalyze the decomposition of peroxide into the reactive oxidants. The transition metal ions were complexed as their hydroxides, which would weaken their oxidation ability and remove them from solution. It is notable that at room temperature, oxidation did not proceed via formation of peroxides and free-radical reactants. Instead, oxidation proceeded via an ionic reaction with charged reactants. [This fundamental difference in the reaction mechanisms suggests that oxidation of paper during artificial thermal aging may not entirely reflect room-temperature natural aging.]


Scientists in the Research and Testing Office, Preservation Office, Library of Congress, describe the relationship between folding endurance and tensile strength of paper, which is relevant for understanding loss of paper strength during aging (Williams et al., 1977; Coffin et al., 2004; Tang and Jones, 1979; Caulfield and Gunderson, 1988; Daniels, 1989; Nissan and Batten, 1990; Padanyi, 1993; Brandis, 1994; Harris, 1995; Havermans et al., 1995; Moropoulou and Zervos, 2003; Karademir et al., 2004; Nondestructive Testing Resource Center, 2010; Popil, R. E., 2010; Alava and Niskanen, 2006). Folding endurance (FE) measures how many times a piece of paper can be folded under a tension load before it breaks. When the paper breaks, its initial tensile strength (TS) at the breaking point has been reduced to the value of the tension load. FE is thus related to the initial TS of the paper, the tension load, and the resistance of the paper to folding fatigue. Of particular interest is that under dry artificial aging, the FE of paper drops rapidly, but the TS remains constant over long aging periods because of the increased crystallinity of the cellulose under dry aging conditions. In contrast, under humid oven aging, there is a rapid decrease in TS and a very rapid decrease in FE, tearing resistance, and bursting strength. FE is the physical parameter that is most sensitive to deterioration of paper, and it is apparently the most revealing physical measurement under both dry and humid heat aging. The article was published in an AIC (American Institute for Conservation) journal with anonymous peer review.

1972


Scientists at the School of Chemistry, University of Leeds, UK, provide data for the hydrolysis species formed when aluminum Al(III) salts are added to water, which is relevant for understanding an important source of acidity in paper. Papermakers alum, which contains Al(III) sulfate, is added during papermaking to aqueous suspensions of pulp and resin during the alum-resin sizing of paper. This does not result in the formation of sulfuric acid, a strong acid, "as is generally stated in library literature" (Smith, 1990). Instead, the Al(III) ions become hydrated, hexacoordinated with six molecules of water, and these weakly acidic hydrates undergo hydrolysis with a pKa of ~ 4-5. This pKa is comparable to that of acetic acid, a weak organic acid that is formed during paper degradation. The article was published in a RSC (Royal Society of Chemistry) journal with anonymous peer review.


A chemist in the Preservation Research and Testing Office, Library of Congress, showed that measurements of paper pH using surface electrode and TAPPI cold extractions had no relationship to the acidity or alkalinity of paper, which is fundamental to evaluating the relevance and meaning of measurements of paper pH in relation to alkaline reserve. Useful examples included one paper that had an alkaline reserve (AR) of 1% CaCO₃, which was in accord with a TAPPI hot extraction alkaline
pH value of 8.7 but not in accord with either surface electrode measurements that showed an acidic pH of 6.4 or a TAPPI cold extraction acidic pH value of 6.15. Another example involved paper that had a highly alkaline surface pH of 9.4 but only had an AR of 0.3-0.6% CaCO₃, unsuitable for permanence. The use of high molecular mass (MM > 200) organic deacidification reagents was considered undesirable because of the large quantity that would be needed for deacidification [such as is needed for the use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008)]. The article was published in conference proceedings with no anonymous peer review.

1970


A scientist at the Institute of Paper Chemistry, Wisconsin, US, presents an excellent introduction to paper, including its history, materials, manufacture, measurable physical and chemical properties and what they mean, factors that impact its durability and permanence, and the use of Arrhenius artificial aging data to try to predict its permanence. The article is written in an easily understandable manner and provides important background for understanding the complexity of paper and why treatments such as mass deacidification are needed. The article was published in conference proceedings with no anonymous peer review.

1968


This PhD dissertation from the Institute of Paper Chemistry, Lawrence University, Appleton, WI provides data for the internal surface area of Whatman # 1 filter paper and two prepared handsheets, which is background chemistry for the proposed use of aminoalkylalkoxysilanes as deacidification reagents (Cheradame 2001, 2003, 2004, 2005, 2006a, 2006b, 2008). The internal surface area of Whatman # 1 was 1.05 m²g⁻¹, and the other two papers had internal surface areas of 1.23 and 1.02 m²g⁻¹. [These data in conjunction with specific wetting surfaces (SWS) provided in Gelest, Inc. (2004) can be used to evaluate the physical meaning of the adsorption data presented in Cheradame (2004)].

1948


A researcher at the Department of Water Supply, Detroit, MI, describes the use of sulfonate dyes for the photometric determination of magnesium. This is relevant for understanding why using the color change of Brilliant Yellow dye as a test of the deacidification efficacy of the Bookkeeper® processes is not a valid indicator of pH (Kidder et al., 1998). Brilliant Yellow changes color from yellow to red in alkaline solutions of magnesium, not because of the alkaline pH but because of the chelation of the magnesium by the sulfonate groups of the dye. [Brilliant Yellow would not be an appropriate choice to use as a pH indicator adsorbed onto paper that inherently or by deacidification contained either magnesium oxide or magnesium hydroxide.] Multiple references are given for the determination of magnesium using color-changing, chelating dyes. The article was published in an ACS (American Chemical Society) Journal with anonymous peer review.