

ACS SYMPOSIUM SERIES **410**

Historic Textile and Paper Materials II

Conservation and Characterization

S. Haig Zeronian, EDITOR
University of California—Davis

Howard L. Needles, EDITOR
University of California—Davis

Developed from a symposium sponsored
by the Cellulose, Paper, and Textile Division
at the 196th National Meeting
of the American Chemical Society,
Los Angeles, California,
September 25–30, 1988



American Chemical Society, Washington, DC 1989



Library of Congress Cataloging-in-Publication Data

Historic textile and paper materials II: conservation and characterization
S. Haig Zeronian, editor, Howard L. Needles, editor

p. cm.—(ACS Symposium Series, 0097-6156; 410)

“Developed from a symposium sponsored by the Cellulose, Paper, and Textile Division at the 196th National Meeting of the American Chemical Society, Los Angeles, California, September 25-30, 1988.

Includes bibliographical references.

ISBN 0-8412-1683-5

1. Textile fabrics—Conservation and restoration—Congresses. 2. Paper—Preservation—Congresses.

I. Zeronian, S. Haig, 1932- II. Needles, Howard L.
III. American Chemical Society. Cellulose, Paper, and Textile Division. IV. American Chemical Society. Meeting (196th: 1988: Los Angeles, Calif.). V. Series

TS1449.H57 1989
746—dc20

89-38410
CIP

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48-1984.



Copyright © 1989

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each chapter in this volume indicates the copyright owner's consent that reprographic copies of the chapter may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per-copy fee through the Copyright Clearance Center, Inc., 27 Congress Street, Salem, MA 01970, for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating a new collective work, for resale, or for information storage and retrieval systems. The copying fee for each chapter is indicated in the code at the bottom of the first page of the chapter.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

American Chemical Society
Library

1155 16th St., N.W.

Washington, D.C. 20036
In Historic Textile and Paper Materials, S. Haig Zeronian, S., et al.; ACS Symposium Series, American Chemical Society: Washington, DC, 1989.

ACS Symposium Series

M. Joan Comstock, *Series Editor*

1989 ACS Books Advisory Board

Paul S. Anderson
Merck Sharp & Dohme Research
Laboratories

Alexis T. Bell
University of California—Berkeley

Harvey W. Blanch
University of California—Berkeley

Malcolm H. Chisholm
Indiana University

Alan Elzerman
Clemson University

John W. Finley
Nabisco Brands, Inc.

Natalie Foster
Lehigh University

Marye Anne Fox
The University of Texas—Austin

G. Wayne Ivie
U.S. Department of Agriculture,
Agricultural Research Service

Mary A. Kaiser
E. I. du Pont de Nemours and
Company

Michael R. Ladisch
Purdue University

John L. Massingill
Dow Chemical Company

Daniel M. Quinn
University of Iowa

James C. Randall
Exxon Chemical Company

Elsa Reichmanis
AT&T Bell Laboratories

C. M. Roland
U.S. Naval Research Laboratory

Stephen A. Szabo
Conoco Inc.

Wendy A. Warr
Imperial Chemical Industries

Robert A. Weiss
University of Connecticut

Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

Preface

EXTENSIVE RESEARCH HAS BEEN PUBLISHED on the chemistry and physics of paper and textiles. From the volume of available work, physical scientists must extract the information required by conservators to assist them in the preservation of fibrous materials. To this end, the Cellulose, Paper, and Textile Division of the American Chemical Society has sponsored four symposia since the mid-1970s on the preservation of paper and textiles of historic and artistic value. These conferences provided a forum where conservators and physical scientists could meet and discuss matters of mutual interest. Papers presented at the first three meetings have been published as chapters in three volumes of the *Advances in Chemistry Series*:

- *Preservation of Paper and Textiles of Historic and Artistic Value*; Williams, John C., Ed.; *Advances in Chemistry* 164; American Chemical Society: Washington, DC, 1977.
- *Preservation of Paper and Textiles of Historic and Artistic Value II*; Williams, John C., Ed.; *Advances in Chemistry* 193; American Chemical Society: Washington, DC, 1981.
- *Historic Textile and Paper Materials: Conservation and Characterization*; Needles, Howard L.; Zeronian, S. Haig, Eds.; *Advances in Chemistry* 212; American Chemical Society: Washington, DC, 1986.

This volume contains chapters from the fourth symposium.

The seriousness of problems related to the conservation of paper is already well recognized. In about 1850, paper became much more susceptible to deterioration because of the acidic nature of the products prepared by the manufacturing processes then being introduced. Today, steps are being taken to correct and prevent problems. The *Wall Street Journal* of March 6, 1989, reported that the publishing industry estimated

that in 1990, 50% of all paper used in book publishing would be acid free compared with only 25% in 1989. According to a report in the March 13, 1989, *Chemical & Engineering News*, acid-free paper is estimated to last 300 years compared with an approximately 30-year lifetime for acidic paper.

The change to alkaline-neutral papermaking is laudable and will assist in the preservation of books published in the future. (The production of alkaline-neutral paper is surveyed in Chapter 1 of this volume.) However, the difficulty with books printed since 1850 remains. Methods of deacidifying paper are critically evaluated in Chapter 2, and the potential of graft copolymerization as a means of strengthening paper is described in Chapter 3.

Another problem conservators face is the deterioration of paper by exposure to light; it is discussed in Chapter 4. Paper is hydrophilic and may turn yellow over time. The importance of controlling the ambient atmosphere in which books are stored is brought out in Chapter 5, and yellowing is discussed in Chapter 6.

Unlike paper, textiles are made from a wide range of fibers formed from different types of polymers. Textiles are usually colored, and the type of dye used depends on the fiber. Thus, each fiber has its own unique set of problems. For example, synthetic fibers are less susceptible to insects than are natural fibers, whose potential for damage depends on the fiber and on the insect. Also, the rate at which fibers deteriorate when exposed to sunlight varies, depending on how they have been dyed and which type of dye has been used. Again, a fiber's susceptibility to a reagent depends on its organochemical nature. Different dyes are susceptible to different reagents as well. Thus, whereas some general rules can be applied to textile conservation, knowledge of the individual fiber, dye, and finish is important.

Currently, the vast majority of textiles being collected by museums are made from natural fibers, and attention is focused on these products in this volume. Silk is discussed in Chapters 7–9, and cellulose in Chapters 10 and 11. Techniques that may be useful for the characterization of textiles to be preserved are described in Chapters 13–15.

One of the fascinations of studying textiles is that in addition to being manufactured from conventional fibers, they can be formed from other materials. Problems related to conservation of a particularly sensitive material, tapa cloth, are discussed in Chapter 12.

The authors wish to thank Sandy Brito for her valuable and prompt assistance with respect to the correspondence generated in the

organization of the symposium and of this volume. We would also like to acknowledge the help we received from Cheryl Shanks and Donna Lucas of the ACS Books Department in the preparation of this book.

S. HAIG ZERONIAN
University of California
Davis, CA 95616

HOWARD L. NEEDLES
University of California
Davis, CA 95616

August 3, 1989

Chapter 1

Permanence and Alkaline-Neutral Papermaking

D. J. Priest

Department of Paper Science, University of Manchester Institute of Science and Technology, Manchester, P.O. Box 88, Sackville Street, Manchester M60 1QD, United Kingdom

The papermaking process is increasingly being modified so that the sheet is formed in a neutral or alkaline aqueous environment, rather than in an acidic one. Paper made in this way is normally longer lasting because acid hydrolysis of the cellulose can no longer occur. However, the reasons for introducing the modified process are largely economic, and the product may not necessarily meet specifications for permanence and durability. This review describes the technicalities of the economic advantages (including easier fibre refining, increased filler content, the use of calcium carbonate fillers, and the availability of cost-efficient neutral sizes), the factors involved in making a change to neutral/alkaline papermaking, and how all this impinges on producing a satisfactory permanent paper.

Paper is essentially a bonded mat or felt of relatively small fibres to which can be added, if required, fillers, wet strengtheners, coatings and so on. Although a paper-like material can be produced from many different polymeric fibres, paper itself is nearly always made using fibres from natural sources, usually, but not exclusively of course, from wood. These natural fibres all comprise polysaccharides of one sort or another, predominantly cellulose, which are very hydrophilic because they contain many accessible hydroxyl groups. The essential adhesion between fibres is a consequence of hydrogen bonds formed through these hydroxyl groups, as is the sensitivity of unmodified paper to disintegration when wetted by water.

In many of its uses, paper needs to have resistance to penetration by aqueous fluids such as writing inks or the damping solutions used in lithographic printing. The treatment given to the surfaces of fibres to make them hydrophobic, which is usually done as the sheet is being formed, pressed and dried on the papermaking machine, is known as "internal sizing", to distinguish it from "surface size" applied on a size press part way down the drying section of the machine.

0097-6156/89/0410-0002\$06.00/0
© 1989 American Chemical Society

Since the early days of machine made paper in the first half of the nineteenth century, the most widely applied method of internal sizing has been the use of naturally occurring resinous materials ("rosins") in conjunction with an aluminium salt, usually aluminium sulphate (called "alum" by papermakers). Various forms of rosin sizes (rosin soaps, rosin emulsions, fortified rosins) have been developed over the years to improve the process, but these variants still involve the use of alum as a means of ensuring that fibres retain a layer of size.

Aluminium sulphate hydrolyses in aqueous solution to yield complex hydrated aluminium ions plus hydroxonium ions (1, 2), and hence a low pH. Papers made using alum/rosin sizing are often said to be "acidic", although this is rather imprecise terminology. A complete definition, following the related TAPPI standard method (3), is that paper acidity is the extent to which water-soluble materials in the paper alter the hydrogen-hydroxyl ion equilibrium of pure water causing an excess of hydrogen ions as measured by a commercial pH meter under specified conditions.

The important point is that the cellulose in these alum/rosin sized papers is susceptible to acid hydrolysis, which results in a lowering of the degree of polymerisation and, eventually, to a serious reduction in the strength of fibres and to complete embrittlement of the paper. Some recent work in the writer's laboratory suggests that when alum/rosin papers are made, the hydroxonium ions which lead to the degradation are adsorbed independently of aluminium ionic species (4).

In recent years, increasing attention is being paid by the paper industry to systems in which sizing is accomplished without the need to have the wet end of the machine running at acidic pH values. In these newer systems the pH may be around the neutral point, or be slightly alkaline due usually to the use of calcium carbonate filler (see below), so they are known as "neutral/alkaline". Papers made in this way do not yield acidic aqueous extracts and hence degrade more slowly (5, 6). Clearly, this is of great significance to those concerned with ensuring that important books and archival documents use paper expected to have a long life, and which will not lead in 30-150 years time to the enormous problems now being experienced in libraries and archives with paper made 30-150 years ago (7). However, it must be recognised that the reasons for introducing neutral/alkaline papermaking were not primarily associated with permanence; papers made in this way do not necessarily meet all the requirements for permanence and durability. Also, the alum/rosin acidic sizing method has been such a dominant force in papermaking that many other features of the process have been designed around it and adapted to it; the often used term "alum/rosin sizing system" is entirely appropriate. Making the change to neutral/alkaline papermaking nearly always involves, as we shall see, much more than throwing a switch or opening a valve.

In a previous publication in this series (8), Hagemeyer set alkaline papermaking in the context of future demand for paper, and dealt briefly with some of the technical consequences. Since then, more mills have converted to the new method, and the aim of this chapter is to inform the reader in some detail about the reasons for changing to neutral/alkaline papermaking, some of the consequences for the production and properties of paper, and how the change impinges on

permanence and durability. It is important for those concerned with conservation and permanence to be able to communicate with papermakers and others with an awareness of relevant problems. Where possible, literature is cited, but a complete review is not intended, and some of the comments arise from the writer's past involvement in some of the industrial aspects of neutral/alkaline papermaking.

REASONS FOR CHANGING TO NEUTRAL/ALKALINE PAPERMAKING. As in most industrial change, the chief incentive is economic, and we need to look at ways in which the neutral/alkaline process gives rise to savings in the cost of production. Four main areas are involved: the fibre furnish, mineral fillers, the sizing system and the papermaking process itself. Although for convenience these will be discussed in turn, it should be noted at the outset that there is a great deal of interaction between the various aspects.

FIBRE FURNISH. It is well established (9) that when fibres are beaten or refined at a neutral or slightly alkaline pH the efficiency of the process is greater than at the acidic pH of around 4.5 common in alum/rosin systems. (When running an alum/rosin system it is inevitable that much of the stock preparation part of the mill operates at low pH because most of the water used is recycled from the wet-end of the paper machine).

The increase in refining efficiency means, for example, that a given level of strength in the paper can be obtained for a lower expenditure of energy. This is a major fundamental economic incentive for converting to neutral/alkaline papermaking, because large amounts of expensive energy are consumed in refining fibres (10). This basic advantage can be exploited in different ways, depending on the particular product being made and market requirements (9).

For example:

- a) The composition of the fibre furnish can be altered. The proportion of hardwood pulp might be increased, for instance, to give a product with the same strength as before, but with improved formation and opacity. Some cheap, relatively weak, bleached mechanical pulp might be introduced, or the proportion already used increased, again giving better uniformity and opacity, and a lower apparent density, but without loss of strength. This latter trend, of course, would not be acceptable in a permanent grade of paper.
- b) The potentially improved strength can be offset by increasing the amount of mineral filler in the paper, and this is a common route to follow, because fillers are usually much less expensive than the fibrous raw materials they replace, whilst at the same time properties such as brightness and opacity are improved. This important aspect is discussed more fully in the next section.
- c) A product of similar composition can be made but simply using less energy in refining.

In fact, these three approaches are not mutually exclusive, and a mill would need to consider how to combine changes to optimise financial savings whilst producing a paper acceptable in quality to the particular market being served.

FILLERS. In addition to being able to use more filler, a very important feature of running neutral/alkaline is the capability of greatly increasing the choice of mineral filler. This is because it becomes easily possible to use fillers constituted from calcium carbonate (CaCO_3), of which there are many different types. In alum/rosin systems, the pH is low enough for chemical reaction with the CaCO_3 to occur, producing troublesome evolution of CO_2 gas, causing froth and foaming and altering the ionic constitution and pH of the wet-end circuits.



Some attempts have been made in the past to overcome this difficulty by pre-treating the slurry of carbonate filler with special starches or water soluble polymers in order to protect the filler particles from acid attack for long enough to avoid foaming etc. (11); if the treated carbonate slurry is added at a suitable point, the dwell time in the acid environment is relatively short. Although these systems can work well if properly set up and controlled, they have not found wide application, largely being superseded by the advent of cost effective neutral sizes, which also avoids the cost of the protecting starch or polymers. However, a parallel development is the availability of rosin size emulsions which are effective at higher pH's (i.e. just on the acid side), and at least one mill in the UK has been taking this approach to using low additions of alum with carbonate filler (12).

Once again, the advantage of being able to use carbonate fillers can be realised in many different ways, depending both on the product and market requirements, and also on the availability and cost of filler supplies. Calcium carbonate fillers are produced either by controlled comminution of naturally occurring materials differing as widely as chalk, limestone or even marble, or by a chemical process leading to "Precipitated Calcium Carbonates", or PCC's. Within each type there are a range of products, varying in particle size and distribution, particle shape, and brightness. Different materials are produced at different locations throughout the world, so affecting detailed local economics. In Europe, there is a plentiful supply of inexpensive ground chalk filler, and there is usually an incentive to replace some or all of the clay (used in an acid sizing system) with chalk, and to increase the total filler content. However, due regard must be paid to relevant properties of the paper; e.g. large proportions of chalk filler will increase the oil absorptivity of the paper and hence its behaviour in printing processes. Also, although the more efficient alkaline beating will generally allow retention of strength at higher filler levels, the relative values of different types of strength can change, leading to possible difficulties in use. For example, if burst and tensile strength remain unaltered, but the paper is not as stiff as before, there is a danger that sheets will not feed properly into printing machines.

In the USA, where there is not the same supply of cheap ground chalks, it may be cost effective to use the more expensive precipitated carbonate, especially if it can be prepared in the mill, as is often the case. Through proper control, it is possible to make fine particle sized uniform products of high brightness, giving the possibility of

replacement, at least in part, of very expensive speciality fillers such as titanium dioxide (13). Use of PCC can sometimes also be justified, even where supplies of cheap chalk are available, when making products involving the use of TiO_2 .

In complete contrast, the choice might be a lower brightness coarser filler where the main aim is cheapening a product without much affecting its optical properties, i.e. employing carbonate only as a filler.

Using appropriate techniques, and for suitable products, it is now possible to make satisfactory papers containing 25-30% w/w of chalk filler, although 15-20% in general neutral/alkaline printing and writing grades is probably more common. Such high levels of filler are not needed for supplying an "alkaline reserve" in permanent grades of paper; the American National Standard for permanence of paper for printed library materials proposes a minimum of 2% as calcium carbonate (14). Although the presence of excess filler is unlikely to be detrimental to permanence, it could mean that the mechanical properties of the paper do not meet the requirements for initial durability - such as those specified in the standard.

SIZING. Clearly, the key to the increased use of neutral/alkaline systems is the availability of suitable cost-efficient sizes. This has come about through the development of synthetic materials which are designed to form chemical covalent bonds with the hydroxyl groups in the surfaces of fibres (13, 15). In addition to the reactant group, the size molecule also has a hydrophobic portion, usually consisting of short alkyl chains. The two types of size in most common use are alkyl ketene dimers (AKD) or alkyl succinic anhydrides (ASA); Figure 1 shows the intended sizing reactions.

In practice several problems have had to be overcome before this apparently attractive method of sizing could be implemented efficiently. Since the ketene or the anhydride have to react with hydroxyl groups, they will also react readily with water; i.e. the molecules are hydrolysed to give non-reacting carboxylic acids (Figure 2). Some means must therefore be found to permit addition of the sizes to the wet-end of a paper machine, and then to ensure that they are retained within the wet paper web in such a way that an adequate size film is deposited on fibres in the dried sheet. This is made more awkward by the essentially hydrophobic nature of the molecules. The means adopted is to prepare emulsions of the sizes, often using cationic starch as a stabiliser and retention aid.

The storage stability of these reactive synthetic size emulsions is also of practical importance; AKD sizes tend to be delivered by the manufacturer in emulsion form, whilst ASA is emulsified on site shortly before pumping it into the wet-end. This is an area where much confidential manufacturer's expertise comes into play.

At one time, difficulties were encountered with ensuring that the desired degree of sizing developed in a reasonable time, especially with AKD's. With rosin/alum, sizing is complete in the reel at the end of the paper machine, but with some early AKD sizes, water resistance continued to develop for some days after the paper was made, making quality control difficult if not impossible. With newer grades of AKD this problem no longer arises, provided care is taken to ensure that temperatures in the drying section of the paper machine are high enough

in the correct positions. The actual mechanism of sizing with these new materials has been the subject of recent studies (16, 17), it seems that only a small proportion of the size actually reacts chemically with the cellulose fibre surface, but that it is essential to add the excess initially. The synthetic sizes tend to be more expensive than rosin, so, neglecting other economies, in a straight replacement they need to be used in smaller quantities; typical addition rates might be 0.5 - 1% w/w of dry fibre. The amount consumed will be related to the type of pulps being used, to the degree of beating and refining, and to the amount and type of filler.

No specific information on the possible effect of the synthetic sizes on permanence is available, and they are not mentioned in the standard (14), but it seems unlikely that they would be deleterious. Presumably they have been used in commercial grades of neutral/alkaline paper subjected to accelerated ageing tests. In terms of general effects on paper, the synthetic sizes have a tendency to reduce the surface frictional properties of paper to a greater extent than rosin. For example, this makes it more difficult to stack piles of cut sheets without slippage. However, the effect is less noticeable when high proportions of chalk filler are used, because the 'blocky' particles increase friction.

THE PAPER MAKING PROCESS

The repercussions of running neutral/alkaline on the total process are widespread and merit a separate article. Whilst in the present context it is not necessary to deal with the topic in detail, to understand the relationship of permanent paper to neutral/alkaline papermaking as a whole, the reader needs to have some appreciation of what it means to change to the new process. In particular, this understanding is very useful for effective communication between manufacturer and user.

To meet this need, brief information is given on each of the relevant main areas of the process:

- the stock preparation, approach flow and wet-end systems.
- formation and drainage on the wire section.
- wet pressing.
- drying.
- size press treatment.
- re-use of broke and waste paper.
- effluent treatment.

STOCK APPROACH FLOW AND WET END SYSTEMS. The papermaking stock being pumped to the headbox contains a number of additives extra to the fibre, filler and size. According to the grade being made, these may include retention aids, dyes or pigments, optical brighteners, pitch control agents and wet or dry strengthening aids. Switching to neutral/alkaline is likely to affect the performance of any or all of these additives. For example, the hue and depth of colour given by dyestuffs is often related to pH, so running alkaline is likely to require changes in the type of dyestuff being used (18). In fact, in planning to change from acid to neutral/alkaline conditions any mill will need to review the nature of all its ancillary materials, and how they are likely to function under the new circumstances. Increased filler levels make choice of retention aids particularly important (19).

Means of ensuring the cleanliness of wet end circuits and approach flow systems will also need attention. Warm suspensions of cellulose fibres and starch are excellent breeding grounds for organisms producing various sorts of unwanted slimes and deposits, and it is customary to add suitable inhibitors. Such growth is often sensitive to pH, and when pH changes different strains of bacteria and fungi become active, requiring different types of slimicide.

To reduce the consumption of fresh water and to minimise volumes of effluent needing to be treated, mills generally seek to run with systems which are as nearly 'closed' as is practicable; i.e. as much water as possible is continuously recycled within the mill. Consequently, increasing quantities of soluble substances are retained within the wet end system. A pH change may once again affect the nature and quantity of these materials, although in general running alkaline may be beneficial here.

Changing to neutral/alkaline conditions can also result in fewer corrosion problems in the wet end systems, a further aspect which has to be taken into account (20).

DRAINING ON THE WIRE SECTION. The differences obtained when beating or refining under neutral/alkaline conditions can produce some unexpected changes in the behaviour of the stock as it drains on the forming fabric of the paper machine - a specially critical region of the process in terms of product quality and uniformity.

At increased levels of carbonate filler, which tends to be more hydrophobic than clay, water drains more readily from the stock, and this is generally an advantage which allows various useful changes. For example, the consistency in the head box can be reduced, to give improved formation and uniformity in the sheet without having to slow down the machine to cope with the extra volume of water needing to be drained.

A key visual indicator of drainage behaviour is the so-called 'dry-line', which is the position down the wire where the sheet of draining stock loses its wet gloss and becomes matt in appearance. When running alkaline the wet web can remain glossy farther downstream, even though the actual solids content has not altered (21). Once this is appreciated, there should be no problem, but it is yet another example of unexpected change.

WET PRESSING. Where wet presses have a plain roll in direct contact with the wet paper web, serious difficulties have been encountered, attributed to hydrolysed and poorly retained neutral size residues (22). These are deposited on the surface of the roll, building up a film to which the wet web adheres, causing wrap rounds and web breaks. If no solution can be found, this would be a big enough problem to preclude running neutral/alkaline; particular attention needs to be paid to minimising pre-hydrolysis and maximising size retention.

DRYING. This is an area where neutral/alkaline papermaking can show advantages, especially when using increased quantities of carbonate filler (21). The hydrophobic nature of the filler, combined with the reduced proportion of hydrated fibre in the web, both mean that drying is more energy efficient. Reducing steam consumption or increasing

machine speeds (where maximum speed was previously dryer-limited) both represent substantial potential economies.

SIZE PRESS. Grades of printing paper, including those for use where permanence and durability are important, are usually treated with starch, or some other water soluble polymer, at a size press part way down the drying section. The degree of internal sizing present in the pre-dried sheet entering the size press helps to control the amount and extent of penetration of surface size picked up. It is very likely when running neutral alkaline that the absorption characteristics of the web at the size press will be different, either because sizing has not developed to the same extent or because of a higher filler level (23) so the process is likely to need modification here too.

RE-USE OF BROKE AND WASTE PAPER. This is an extensive and complex area which can only be touched on here. (Broke is the term used for paper made on a machine which does not end up in the finished reel; edge trims, waste at reel changes etc.). Examples of relevant factors are:

- a) It is very difficult to run acidic broke or waste in an alkaline system (21).
- b) One incentive for changing from acid to neutral/alkaline conditions can simply be the need to run the paper or board machine using a proportion of broke from, for instance, an associated paper coating plant employing a calcium carbonate pigment.
- c) Papers sized with neutral reactive sizes are sometimes more difficult to disintegrate in broke pulpers.
- d) In a multi-machine mill where only one machine was making an archival grade, it would probably be necessary to segregate the broke from that machine, to ensure that broke from other machines was not used. This is often not a normal procedure and generates added cost.

EFFLUENT TREATMENT. Again, this is a complex matter, and circumstances will differ from mill to mill, depending on product and situation. Two features of some importance are:

- a) Running neutral/alkaline is said to allow mills to operate with a highly closed system because there is less dissolved material to accumulate, and this means a lower volume of effluent to treat.
- b) Absence of alum, which is a very effective flocculant for suspended solids, means that an alternative cost-effective synthetic flocculant will be required for the effluent treatment plant.

PROPERTIES AND PRICE. Because of the wide range of grades of paper and paperboard being made both acid and neutral/alkaline, it is not possible to generalise on the effect of a process change on paper properties. If a single grade is made by either method, and filler levels or furnish have not been changed, there are unlikely to be any distinctive differences in general physical properties (but recall the surface frictional effects mentioned above) - indeed, the new neutral/alkaline grade would be required to meet the same specification.

However, it is clear that in one very important respect the two papers would be different, and that is in their response to accelerated ageing tests. Where permanence is required, the advent of neutral/alkaline sizing has enabled satisfactory grades to be made in a way not previously possible. Running neutral/alkaline, as we have seen, is only one aspect of permanence; attention must still be paid to having the right quality of fibre (excluding all lignin for example), and including amounts of carbonate filler which will act as an alkaline reserve, but will not be present in sufficient quantity to adversely affect the properties of the paper (14).

Again, in considering the price to be paid for paper, it is vital that the correct comparisons are made. If a standard commodity grade of neutral/alkaline sized paper, made in large tonnages, meets the required specification for permanence, it should clearly cost no more than the corresponding acid sized paper. Even if it does not meet a set permanence specification, it is very likely to be considerably better in this respect than the acid sized grade it has replaced.

On the other hand, if a special archival grade is being made to order and a tight specification, in small tonnages, with a non-standard expensive fibre furnish, on a small slow machine which needs a special cleaning before the making, then the paper is likely to be equally expensive whether it is made acid or alkaline. Either way, it will still cost more than the high tonnage standard commodity grade.

CONCLUDING REMARKS

The prospects for improving the longevity of paper in books, documents and archives has been greatly enhanced by the introduction of practicable cost effective systems of neutral/alkaline papermaking. In many ways, the problems are now in the techno-economic and marketing fields - every effort needs to be made to ensure that those responsible for specifying the paper to be used for books, archives and so on, are fully informed about the merits of the various grades of neutral/alkaline paper now available for selection. The contents of this article are intended to make a positive contribution as a source of relevant information, because it is undoubtedly important for those concerned with purchasing paper for permanence to be aware of how such paper relates to the wide field of general neutral/alkaline papermaking.

LITERATURE CITED

1. Arnsion, T.R.; Stratton, R.A. TAPPI (1983) 66, 72.
2. Strazdins, D. TAPPI (1986) 69, 111.
3. TAPPI Official Test Method, T 509 om-83 (1983).
4. Priest, D.J.; Farrar, M. 'Symposium 88' proceedings, Canadian Conservation Institute, 1988.
5. Tosh, C. Paper (1981) 195, 26.
6. Selawy, A.C.; Williams, J.C. TAPPI (1981) 64, 49.
7. Fifield, R. New Scientist (9 April 1987) 31.
8. Hagemeyer, R.W. In Preservation of Paper and Textiles of Historic and Artistic Value II; Williams, J.C., Ed.; American Chemical Society, Washington, 1981; 241.
9. Breslin, J. Paper Trade Journal 1985, 169, 57.

10. Smook, G.A. 'Handbook for Pulp and Paper Technologists', TAPPI/CPPA; 1982; 181ff.
11. Brooks, K.; Shiel, L.E.; Smith, D.E. U.S. Patent 4 272 277, 1981.
12. Roberts, F.J.; Wilson, C.M.W. In Trends and Developments in Papermaking; Evans, J.C.W., Ed.; Miller Freeman Inc.: San Francisco, 1985; p 15.
13. Brink, H.G.; Gaspar, L.A. TAPPI Seminar Notes, Alkaline Papermaking (1983) 15.
14. Permanence of Paper for Printed Library Materials, American National Standard, ANSI Z39, 48-1984, .
15. Alberts, A.M. TAPPI Seminar Notes, Alkaline Papermaking (1983) 35.
16. Davison, R.W.; Hirwe, A.S. TAPPI Alkaline Papermaking Seminar Notes (1985) 7.
17. Roberts, J.C.; Garner, D.N.; Akpabio, U.D. In Papermaking Raw Materials; Punton, V., Ed.; Mechanical Engineering Publications Ltd., London, 1985; Vol. 2, p 815.
18. Westmoreland, J.; Majunclar, A. In Trends and Developments in Papermaking; Evans, J.C.W., Ed.; Miller Freeman Inc., San Francisco, 1985; p 99.
19. Atkinson, J.G. Paper Trade Journal 1982, 166, 30.
20. Bowers, D.F.; TAPPI (1986) 69, 62.
21. Beach, C.M.; TAPPI Seminar Notes, Alkaline Papermaking (1983) 75.
22. McNamee, J.P.; *ibid*, p. 73.
23. Bryson, H.R. Paper Trade Journal 1978, 162, 26.

RECEIVED February 22, 1989

Chapter 2

Critical Evaluation of Mass Deacidification Processes for Book Preservation

David N.-S. Hon

Wood Chemistry Laboratory, Department of Forestry, Clemson University,
Clemson, SC 29634-1003

Four mass deacidification processes for book preservation; namely, the Library of Congress diethyl zinc process, Wei T'o nonaqueous process, Kopper's "Book Keeper" process, and Langwell interleaved vapor phase process, are critically evaluated, based on their chemical characteristics and effectiveness on deacidification.

The collections of America's libraries are deteriorating rapidly. Thousands of books have already disappeared; millions are in grave danger. On March 29, 1987, The New York Times published an article with an attention getting title: "Millions of Books are Turned to Dust - Can They Be Saved?" (1) This title summarized explicitly the actual situation in libraries and archives in North America and Europe. The inherent acidity of book papers is the major cause of deterioration. In order to salvage a book, acid must be neutralized with alkaline chemicals. The neutralization process is called deacidification. Ideally, the process will also deposit an alkaline reserve to prevent future acid attack. Many deacidification processes have been developed since the 1960s (2-4). Several of these have also successfully demonstrated their potential and the possibility of operating them on a pilot or a commercial scale. In this review, a critical evaluation of these mass deacidification processes is made. The problems of acid deterioration of modern papers, development of deacidification processes, their chemical characteristics and effectiveness, as well as the need for the development of an integrated paper preservation program are discussed.

The Fate of Modern Papers

The cave paintings of Paleolithic man, the hieroglyphics chiseled into the crumbling antiquities of ancient Egypt, and the rune-covered artifacts of Scandinavia and Northern Europe were to preserve forever their activities and cultural heritage. Today, for the same purpose,

0097-6156/89/0410-0013\$06.25/0
© 1989 American Chemical Society

we record our knowledge, technology, activities and culture on paper. Although the cave paintings of Cro-Magnon man which were made 35,000 years ago are still in good condition, ironically, modern paper which was made less than one hundred years ago is crumbling in libraries throughout the world.

The facts are that of the 20 million books and pamphlets in the collection of the Library of Congress, as many as 30% are in such a critical stage of deterioration that they can not be circulated (5,6). A recent survey of the New York Public Library revealed that nearly 50% of its more than five million books are on the brink of disintegration (7). This phenomenon can be observed in any major university or research library. Millicent Abell of Yale University Library has estimated that as many as 76 million books nationwide may literally be crumbling into dust, with more joining the list every year (8). A study conducted by William Barrow sadly indicated that 97% of all books published between 1900 and 1949 would have a useful life of fifty years or less (9).

Why are the cave paintings of thousands of years old in better condition than modern papers? Why do many early books printed in the 15th century show no signs of serious deterioration? How can we preserve our accumulated knowledge? Are the current technologies on book preservation effective? Are the current practice on book preservation acceptable?

The objective of this report is to attempt to answer these questions. Evaluation of current technologies on mass deacidification processes are the main thrust of this work. In addition, the need of an integrated, complete book conservation program is discussed.

Before embarking on any discussion on mass deacidification, the history and development of paper making and causes that lead to deterioration of modern paper are reviewed.

History and Development of Paper Making (10)

Paper, one of man's most essential commodities, was first made in the Orient about 2,000 years ago. Credit for the invention of paper has been given to T'sai Lun, a member of the Imperial Guard and Privy Councillor, who conceived the idea of making paper from old rags, flax, hemp, rice stalks and tree bark (11). The Chinese macerated fibers from these materials in water and drained the suspension on a mold covered with silk cloth. The fiber mats were removed and dried in the sun to form paper. This uniqueness is attested to by its slow communication to other parts of the world: five hundred years to reach Korea and Japan; six hundred years to Samarkand and the Arab world; and one thousand years to Europe, and even later to America in 1690. During that period, rags of cotton, flax, jute, and hemp comprised the sole source of raw materials used in paper manufacture.

From the advent of papermaking, the use of rags or bast fibers grew rapidly prior to 1800, creating a shortage of papermaking raw materials. It has been reported that during that period, even linen shrouds from exhumed corpses were sold for papermaking (12). In 1719, Rene de Reaumur, a brilliant French scientist, suggested that paper could be made from the fibers of plants without using rags or linen. However, it took until 1764 for a German clergyman, Dr. Jacob Scaffer, to make paper experimentally from a wide variety of plant