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The Impact of the Florence Flood on Library Conservation in the United States of America

A Study of the Literature Published 1956–1976

By SHERELYN OGDEN

Contents

1. Introduction

The Florence flood of November 4, 1966 is asserted by prominent library conservators to be a turning point in the development of conservation in the United States. Paul N. Banks, Conservator of the Newberry Library, and Peter Waters, Restoration Officer of the Library of Congress (LC), frequently have asserted that library conservation has a Biblical nature, that is, conservators tend to view the field in terms of "before the flood" and "after the flood." In 1970, Waters expressed his hope that the salvage activities which immediately followed the flood would come to represent "a turning point in ... thinking about book conservation."[1] (p. 69). George M. Cunha, Director Emeritus, New England Document Conservation Center (NEDCC), said in 1975:

Things have been changing, dramatically, in the last few years ... beginning with the tragic and newsworthy floods in Florence in 1966. Television and radio news coverage made a big to do about

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it. The National Geographic Magazine printed a long, illustrated article on the flood and the drama was kept in the public eye for many, many months. This focused international attention on the problem of conservation, made people begin to think about such matters, and was the turning point from which things began to look better[2] (p. 22).

Indeed library conservation has changed in the years since the flood, but the question of whether the flood represents a turning point or change in direction has not been examined. The purpose of this study is to determine the nature of the changes and the impact of the flood on the development of conservation in the United States. By more fully understanding the changes, conservators and librarians may be able to identify what the trends in library conservation mean in terms of the availability of library materials in the future.

The technique followed in this study is review and evaluation of the literature of library conservation written prior to and after the flood. The literature examined is limited to publications issued between 1956 and 1976, the ten years prior to the flood and the ten years after the flood. The ten-year periods were chosen because a decade is judged as sufficient time for changes to become evident and not so much time as to be unmanageable. Also, this particular twenty year period can be considered to represent the real-life-time of library conservation since relatively little occurred in the field prior to 1956. However, the scope of the study is not rigidly restricted to the twenty year period; when a work of significance was found which lies outside the allotted period, it was included.

A description of the Florence flood is not included because of space limitations and because most conservators and librarians are familiar with the flood. A discussion is included in the author's M.A. thesis: "*A Study of the Impact of the Florence Flood on the Development of Library Conservation in the United States: 1966–1976*," Graduate Library School, University of Chicago (available through the Photoduplication Department, Joseph Regenstein Library, University of Chicago, Chicago, Illinois, 60637).

The sources used in the study were gathered from the following bibliographies and indices: Paul N. Banks, *A Selective Bibliography on the Conservation of Research Library Materials* (Chicago: The Newberry Library, 1978); George Martin Cunha and Dorothy Grant Cunha, *Conservation of Library Materials: A Manual and Bibliography on the Care, Repair, and Restoration of Library Materials* (Metuchen, New Jersey: The Scarecrow Press, Inc., 1971); International Institute for Conservation of Historic and Artistic Works, *Art and Archaeology Technical Abstract* (New York: Institute of Fine Arts, New York University, for The International Institute for Conservation of Historic and Artistic Works, 1955 sq.); *Library Literature* (New York: H. W. Wilson, 1933/35 sq.); Frederick L. Rath, Jr. and Merrilyn Rogers O'Connell, *Care and Conservation of Collections*,

compiled by Rosemary S. Reese, (Nashville, Tennessee: American Association for State and Local History, 1977); and Richard D. Smith, bibliography for course nr. 348, "Conservation of Library Materials," Graduate Library School, University of Chicago. Specialized sources, such as the annual reports of the Association of Research Libraries, the Council on Library Resources, Inc., and the Library of Congress, were also checked for relevant information. Only works actually cited are listed in this publication. The complete list of about 350 pertinent works consulted is given in the author's M.A. thesis cited above. These works were selected from an initial bibliography of 450 works which is obtainable from the author.

The definitions of special terms or concepts are given where the term is first used. "Library conservation" as used in this study is limited to books. Microform, maps, manuscripts and other forms of library materials are, for the most part, excluded. The definition includes (1) standards for and philosophy of physical treatment, (2) scientific investigation in deterioration and preservation, and (3) techniques of physical treatment. Both the preservation of books of value for informational content only and the preservation of books of value as cultural artifacts are included.

The principal criteria used to evaluate whether the Florence flood caused a change in library conservation are: (1) principles and standards of treatment, (2) science in conservation, and (3) physical treatment. These criteria are defined and the literature evaluated under titles 2, 3, and 4. Those publications believed to best represent the field were studied to define the state of the art prior to the flood and subsequent changes. The conclusions from this examination are presented under title 5.

2. Principles and Standards of Conservation Treatment

2.1 *Principles*

Library materials, our cultural heritage, belong not only to the present legal owners but to all mankind, including future generations. These materials must receive proper conservation treatment if they are to remain available for future generations. Because the consequences of no or inadequate treatment may not become apparent for years, a long-term perspective involving a sound ethical and philosophical basis for decision making in the treatment of library materials is important.[3] (p. 217). The literature examined indicates that the basis for the decision making process is evolving but has not yet been fully developed. However, four specific principles of conservation treatment warrant enumeration.

(1) The artifact should not be altered any more than necessary for its preservation. In 1956, Lindberg wrote:

> In its unrepaired state a damaged old binding may give useful information on early binding methods. It may therefore be best to keep it as it is, well protected in a flannel-covered box, only cleaning the leather.[4] (pp. 317–8).

Frequently, however, a book must receive extensive physical treatment – such as rebinding – causing it to be significantly altered.

(2) All fragments of the original binding should be retained and all work thoroughly documented if the book has value as an artifact. As Cockerell asserted in 1960 in *The Repairing of Books*, "every contemporary part of a valuable book and binding must be preserved."[5] (p. 40).

(3) Materials used in treatment should be as permanent and durable as appropriate to their use. Numerous references appear in the literature both before and after the flood suggesting that the concept of permanence and durability may be the most widely recognized and applied principle.[6–12]

(4) Another principle is reversibility which implies that the conservator should be able to undo or reverse any conservation treatment.

Banks recently stated that these ideal principles "can never be fully attained for any book, and the degree to which they will be attained is usually related to the value of the book."[3] (p. 213). He asserted elsewhere that "the compromises which have to be made should be made with them as a basis."[7] (p. 127). As Alden pointed out with regard to this about seven years prior to the flood, "a reasonable balance must be maintained between this ideal and the widest possible usefulness of the book itself.[13] (p. 272).

2.2 *Standards*

Standards are a means of maintaining a uniform and suitable level of treatment. Unfortunately, no agreed-upon conservation standards exist for the treatment of most categories of library materials. The Library and Archives Committee of the National Conservation Advisory Council (NCAC) described the situation:

> Standards of adequate and proper conservation treatment would appear to be the most direct and impersonal means of protecting books and manuscripts. However, there are virtually no standards of this type.
>
> The reasons for this lack of treatment standards are numerous and not difficult to find; the diversity of materials needing treatment, lack of suitable methods for many problems, economic and commercial strictures, the general underdevelopment of the field, and so on. Another significant reason is undoubtedly the lack of a suitable body to come to grips with this difficult problem.[14] (p. 39).

Library materials can be categorized according to their value or significance when standards of treatment are being considered. The two most frequently used categories are materials valuable for informational content only and materials valuable as artifacts.

Cunha and Cunha pointed out that no generally accepted standards of treatment for materials of value as artifacts were in existence in 1970:

> There are no established standards for the total restoration of rare and valuable books, although the Standards of the Guild of Book Workers . . . are reliable general guidance for quality binding workmanship. There is no policing organization overseeing professional performance of restorers and conservators, although those who are members of the American Group of the International Institute for Conservation can be assumed to subscribe to its [Pease] code of ethics.[15] (v. 1; p. 141).

The situation is essentially the same today. Furthermore, neither the standards of the Guild of Book Workers nor the Murray Pease Report/Code of Ethics for Art Conservators is directly applicable to the needs of library conservation. The Guild of Book Workers' standards are intended to govern work submitted for exhibition and as such are more suitable to the work of designer or art binders than conservation binders. The Murray Pease Report/Code of Ethics is slanted toward conservators of art objects. It does not take the needs of other conservators, such as library conservators who must deal with large numbers of items, into consideration. It is presently undergoing revision and some of the biases may be eliminated. About 1975, the International Federation of Library Associations issued its "Rules for Restoration Work."[16] These rules are not accepted as a suitable standard by the NCAC Library and Archives Committee because their wording is so general they allow for inadequate or inappropriate treatment.[14] (p. 40).

Despite the lack of generally accepted standards for materials of value as artifacts, standards exist for materials valuable for informational content only. The first, produced in 1923, was entitled "General Specifications for Library and School Book Binding" and was prepared jointly by the Commitee on Bookbinding of the American Library Association (ALA) and the Library Group of the Employing Bookbinders of America.[17] (p. 10). In 1933, the ALA and the Book Manufacturers' Institute (BMI) issued "Minimum Specifications for Class 'A' Library Binding." After the library binders withdrew from the BMI and formed the Library Binding Institute (LBI) in 1935, a joint committee of the ALA and the LBI had responsibility for the "Minimum Specifications" and amended it in 1938 and 1952. In 1954, the joint committee was dissolved. By 1956, the "Minimum Specifications" had become the most widely accepted standard for library binding.[17] (pp. 11–12) The LBI's "Library Binding Institute Standard for Library Binding" is based upon it.[18] (p.

1). This LBI standard, now considered the authoritative version by most librarians, represents:

> The best judgment of Certified Library Binders of the minimum specifications necessary to produce a volume which will achieve two objectives: first – meet the requirements of libraries for an end product capable of withstanding the rigors of normal library circulation or use, and second – provide maximum reader usability.[17] (p. 67)

In 1939, the ALA and the LBI approved "Standards for Reinforced (Pre-Library-Bound) New Books." This standard was also incorporated by the LBI into its "Library Binding Institute Standard for Library Binding."[18] (p. 1). "Minimum Specifications for Bindings for Lesser Used Materials for Libraries," referred to as "LUMSPECS," was issued by the ALA in 1957 and approved by the LBI the same year. The purpose of these specifications is to provide a method of binding for materials which do not warrant a Class "A" binding but which do warrant more protection than that supplied by a pamphlet case.[19] (p. 51). Another standard is the "Official Minimum Manufacturing Standards and Specifications for Textbooks" which was developed for use by Textbook publishers.[17] (p. 13).

These binding standards are defined by particular materials and methods. The belief, when the early standards were written, was that the only assured way to obtain a product which would perform satisfactorily was to control materials and techniques used in manufacturing. Since that time, materials and methods have changed, and these inflexible standards do not allow application and use of new, improved materials and methods.[17] (p. 2). The ALA decided that new, more flexible standards oriented toward library requirements were needed.

In 1960, the Council on Library Resources, Inc. (CLR) awarded a nearly $ 19,000 grant to the ALA's Library Technology Project for the development of "performance" standards. Three performance standards – one each on durability, workmanship, and openability – were produced. Two testing devices were designed for measuring binding performance – the Universal Book Tester and the Openability Test Plate.[17] (p. 2). This project resulted in two publications – *Development of Performance Standards for Library Binding, Phase I* and *Phase II*.[20,21] In 1967, the ALA approved these statements as its official standard and in 1973 withdrew the endorsement of the "Minimum Specifications for Class 'A' Library Binding."[18] (pp. 1–2). This withdrawal of endorsement resulted in clarifying discussion between the LBI and ALA. The ALA does not believe the new standard to be the ultimate one and recognizes that the LBI standard produces a durable book. But, according to *Book Production Industry:*

> With newer bindery equipment, technologies and materials, the ALA argues, there is no need to remain tied to a standard based on a prescription; rather, there should be a standard based on how well the binding does the job.[22] (p. 54)

A difficulty with all the standards is that they tend to be applied not only to books of value for informational content, for which they are intended, but also to books of value as artifacts, for which they are not considered appropriate by library conservators.

Clearly more standards are needed – standards which will protect books as cultural artifacts. As Roberts asserted:

> The present binding standards seem more applicable to those libraries that do not have, and have no intention of maintaining, historical collections. A library that discards old editions in favor of new editions, that does not intend to keep more than say five years of a periodical title, or that weeds its collection of uncirculated books is in no way similar to the research library – academic or public. The binding requirements of the two are entirely different and their standards should and must be different.[23] (p. 23)

This review of the literature indicates that the current principles and standards of treatment in library conservation have been in existence for the last twenty years. The principles of conservation treatment followed today were put forward before the flood. However, the increased number of post-flood references to these principles indicates that they were discussed, critically evaluated and applied more often after the flood. This is because the Florentine salvage operation raised the level of awareness of the importance of conservation and, as discussed below, prompted the evolution of ideas of what constitutes certain conservation treatments. The only specifications which are applicable to library conservation and which qualify as standards are those guiding the binding of material valuable for informational content only. These specifications existed or were in the process of development before the flood.

3. Science in Conservation

3.1 *The W. J. Barrow Research Laboratory, Inc.*

The Barrow Research Laboratory is the only research facility which published regularly in the library and conservation literature during the period studied. Barrow (1904–1967) became interested in the deterioration of library materials when, in the course of studying his family history, he encountered many old books and documents which either had been repaired or were in need of repair.

He studied bookbinding and document restoration methods and, in 1932, established a document restoration shop. In 1935, he began research on the deterioration of paper.

In an attempt to lower the costs of methods of lamination being studied at the National Bureau of Standards, Barrow developed the "first practical roller-type laminating machine" for application of cellulose acetate film. Later he strengthened the laminate produced by including a sheet of tissue on each side of the document improving tear resistence and folding endurance. While he continued development of the laminating process, he began experimentation with procedures to neutralize acidic documents prior to lamination to reduce the rate of deterioration. Early studies by other investigators led Barrow to develop the calcium hydroxide/calcium bicarbonate deacidification process by the mid-1940's.[24] (p. xii).

In 1955, Barrow published *Manuscripts and Documents: Their Deterioration and Restoration* in which he recorded information from historical sources on factors which govern permanency and deterioration in documents; he discussed the effects of some inks on paper, how and from what materials paper has been made, and which components of paper have contributed to its preservation and which to its deterioration.[8] In May 1957, the CLR awarded the Virginia State Library a grant for investigation of the deterioration of modern book papers; the findings were presented in *Deterioration of Book Stock: Causes and Remedies: Two Studies on the Permanence of Book Paper Conducted by W. J. Barrow.*[26] The first study established that the physical condition of books thirty to sixty years old was worse and the rate of deterioration greater than librarians had previously assumed. The second study developed procedures to alleviate this deterioration; these deacidification procedures involved soaking materials in saturated solutions of calcium and magnesium bicarbonates. A subsequent CLR grant was awarded in March 1959 for development of specifications for a permanent and durable book paper and of an economically feasible manufacturing method. *The Manufacture and Testing of Durable Book Papers Based on the Investigations of W. J. Barrow* reported that six experimental and two commercially manufactured papers were produced; they were claimed to be competitive in price, proven to be initially durable, and tested to demonstrate a life expectancy of more than four hundred years.[27]

In August 1961, the CLR funded the establishment of the W. J. Barrow Research Laboratory, Inc., a new facility separate from the W. J. Barrow Restoration Shop, Inc. The laboratory was located in the Virginia Historical Society in Richmond. Work began on spray deacidification of bound and unbound volumes and investigation of aging properties of polyvinyl acetate adhesives. In February 1962, work commenced on development of performance

standards for library binding. *Permanence/Durability of the Book: A Two-Year Research Program* (1963) reported progress on these projects and was the first of seven publications in the series *Permanence/Durability of the Book.*[28] Later publications described work done in evaluation of accelerated aging tests, development of faster methods of deacidification, evaluation of polyvinyl acetate adhesives used in library binding, development of spot tests for groundwood, high acidity, and alum-rosin size in paper, and permanence and durability of papers from 1507 to 1949. The laboratory also investigated the maximum safe pH for paper, effect of temperature on rate of deterioration, methods of strengthening paper while deacidifying it, effects of sea water on permanency of early rag paper, and development and field testing of a morpholine vapor-phase deacidification process.[29,30]

The CLR, providing over one million dollars, was the major source of support for the Barrow Research Laboratory between 1961 and 1977. The Laboratory closed when the CLR withdrew support because of other obligations and the increasing costs of the Laboratory. Most of the equipment from the Laboratory was loaned permanently to the Center on the Materials of the Artist and Conservator, Carnegie-Mellon Institute of Research, Pittsburgh; the books used as samples in early studies were given to the Library of Congress.[31] (pp. 45–6).

3.2 *Other Research Facilities*

The Barrow Research Laboratory was not the only research facility doing work in library conservation.[87] Unfortunately, information regarding the work of the other facilities is incomplete in the conservation and library literature reviewed. For example, the Institute of Paper Chemistry, Appleton, Wisconsin, made valuable contributions in terms of research, publications, and educational programs, yet few references appear.

The Paper Section of the National Bureau of Standards (NBS) has conducted research relevant to library conservation for over fifty years. The number of reports issued each year between 1929 and 1976 indicates that periods of greatest activity were the thirties and late sixties and seventies. In the thirties, twenty-eight reports were issued as articles in technical journals or as government documents, and from 1966 through 1976, thirty-six reports were issued. During the twenty-six intervening years, however, only eighteen reports were produced. Research was conducted on: different methods of measuring the pH of paper; techniques and materials used in lamination; degradation of cellulose; evaluation of the stability of different types of papers; development of specifications for archival record and storage materials; and identification of a source of error in pH determinations of paper. An on-going project is a study of accelerated versus natural aging of paper (Appendix 2). Another project is a paper research program cooperatively developed by the NBS, the Society of American Archivists and the National Archives and Records Service. The project, which began around 1969, now appears to be defunct since money in the special support fund has been disbursed.[32–34]

Establishment of the Preservation Research and Testing Office of the Library of Congress, in planning in January 1966, was emphasized in the reorganization of LC's preservation program in 1967. The Library of Congress received a grant from the CLR for equipment to set up the laboratory in 1970. In January 1971, Williams was hired as Research Officer and Director of the laboratory, and research began in spring, 1972.[35] (p. 15),[36] (pp. 106–7),[37] (pp. 118–9),[38] (p. A8).

The laboratory is responsible for "... pure research into the fundamental aspects of preservation problems, applied research, and testing and quality control of supplies used in the preservation of library materials."[39] (p. A165). Research includes evaluation of currently used methods of deacidification, investigation of restoring strength to deteriorated paper by graft polymerization, examination of properties (uses, types, shelf life, methods of formulation) of adhesives used in library conservation, and analysis of conditions (light, atmospheric contaminants) which contribute to the deterioration of paper.[39] (pp. A165 – A166).

An important responsibility of the Preservation Office of LC is assistance in the informational needs of librarians at other institutions in the United States. This responsibility is met through seminars, workshops, and lectures conducted by members of the staff and through reports and papers. The reports and papers are issued in the form of published leaflets, working drafts, and workshop notes. They range in coverage from a broad approach to conservation, as in the preservation leaflets on *Selected References in the Literature of Conservation* and *Environmental Protection of Books and Related Materials*, to description of specific techniques, such as "The Deacidification and Alkalization of Documents with Magnesium Bicarbonate" and "Heat-Set Tissue Preparation and Application" (Appendix 1). The Preservation Research and Testing Office is responsible for producing in part several of these reports and papers. Also, members of the staff of the laboratory have developed new techniques or modified existing techniques for the deacidification of paper which have been patented, and one member edited an American Chemical Society monograph on the conservation of paper and textiles.[40–43]

Since the Barrow Research Laboratory ceased operation, the Preservation

Research and Testing Office has become the best known facility in the United States conducting research in the conservation of library materials. A significant aspect of the LC laboratory is that the staff scientists work in close cooperation with conservators. As explained in "Preservation Supplement 72–3" of the *Library of Congress Information Bulletin:*

> ... The research staff and the conservation workshop staff have an opportunity to work side by side, to exchange ideas, and to test many of the results of the research program in the practical environment of the workshop. At the same time new techniques and procedures developed in the workshop can be scientifically evaluated in the laboratory. This cross fertilization of ideas should lead to a strong, viable research program capable of developing sound solutions to the vexing preservation problems which beset librarians and archivists of the 20th century.[39] (p. A168)

3.3 Current Methods of Deacidification

One of the most pressing problems for conservators is acidity in paper. The problem is huge quantitatively and, unless cost-effective deacidification treatments are developed, significant portions of library collections will be lost. The applications of science to conservation appearing most frequently in the literature is deacidification, that is, neutralization of acid present in paper and deposition of a buffer to prevent reacidification in the future.

Innumerable articles have appeared in the literature discussing deacidification processes. Smith explained that aqueous deacidification treatments are derived from work of the Canadian Schierholtz who received a patent in 1936 for a *Process for the Chemical Stabilization of Paper and Product.*[44] Schierholtz treated paper with aqueous solutions of barium, calcium, or strontium bicarbonates or by hydroxides of these followed by a carbon dioxide treatment to convert hydroxides to carbonates.[45] (pp. 66–7). Barrow became acquainted with the work of Schierholtz and applied it to deacidify documents before laminating them. He originally used a calcium bicarbonate method but, by the mid-1940's, developed the two-shot calcium hydroxide/calcium bicarbonate method mentioned above.[24] (p. xii),[45] (p. 68). This process was the primary process used during the forties and early fifties. In 1956, the Document Reproduction and Preservation Branch, U.S. National Archives and Records Service, introduced the one-shot magnesium bicarbonate immersion treatment.[45] (pp. 69–70). The aqueous process followed by most conservators today is derived from this treatment. In 1959, Barrow recommended use of calcium and magnesium bicarbonates for deacidification by overnight immersion. In 1964, scientists at the Barrow Research Laboratory considered deacidification agents other than calcium and magnesium but made no recommendations. A preliminary paper on recently completed work at the Preservation Services Laboratory, U.S. National Archives and Records Service reported the advantages of using magnesium hydroxide as the starting material for preparation of magnesium bicarbonate deacidification solution.[46] The complete report, entitled "Preparation of Solutions of Magnesium Bicarbonate for Deacidification of Documents," will be published in an upcoming issue of *Restaurator*.

Aqueous deacidification is the method most conservators use to neutralize acid present in paper. However, aqueous deacidification is costly in terms of time and hence money, and many materials cannot be treated because they contain inks or colors which are soluble in aqueous solutions. An alternative to aqueous deacidification is organic solvent-based deacidification. Organic solvent-based deacidification processes alleviate the problems of aqueous treatments to a great degree, and accelerated aging studies indicate that nonaqueous deacidification treatments improve the stability of acidic paper at least as efficiently as aqueous treatments.[47] (p. 159). Inks and colors which are soluble in water-based solutions are usually not soluble in organic solvents. These solvent-based systems are more readily adaptable to time-saving application procedures which makes them less costly than aqueous processes even though the components are more expensive.

Smith developed an organic solvent-based deacidification solution at the Graduate Library School, University of Chicago. The original solution contained alkoxides of alkali and alkaline earth metals dissolved in alcohols and chlorofluorohydrocarbon solvents (Freon) and was designed for application by immersion, spraying or brushing. Smith's process was improved by Kelly at the Preservation Research and Testing Office of the Library of Congress who combined the preferred deacidification agent, magnesium methoxide, with carbon dioxide gas to form methoxy magnesium methyl carbonate (MMMC). MMMC reacts less readily with water vapor, and its solutions are more stable than magnesium methoxide solutions under conditions conservators use to deacidify paper.[48]

A variety of other deacidification processes have been proposed in the literature but appear to be out of favor with most conservators. Kathpalia began work on an ammonia process in 1956 and published a description of it in 1962.[49] The effect of the treatment is claimed to be transient because the ammonia volatilizes from treated materials.[45] (p. 73). However, at the annual meeting of the Society of American Archivists held in 1976, Kathpalia stated that the treatment is not transient and has an extended lifetime under Indian library conditions.[48] In 1964, Langwell published information on his Postlip Duplex Lamination process.[50] This process is a combination treatment intended to deacidify and strengthen at the same time. The object to be treated is

heat laminated with a tissue which has been coated with an adhesive which contains the deacidification agent magnesium acetate. Information was published by Langwell on the Vapor Phase Deacidification (VPD) process in 1966.[51] In this treatment, books and documents are exposed to the deacidification agent cyclohexylamine carbonate (CHC). Many conservators are reluctant to use CHC because it is reported to cause papers to discolor and to be hazardous to persons coming in contact with its vapors; furthermore, its long-term effectiveness is questioned.[47,52,53,54]

References to the Raff, Herrick, and Adams sodium carboxymethyl-cellulose combination method of deacidification began to appear in 1966.[55–57] Paper to be treated is impregnated with a solution of water, sodium carboxymethyl-cellulose, and a wet strength resin. Another combination treatment is the Regnal Process, the development of which began about 1955.[48] Materials are treated with a biocide, a strengthening agent, and the deacidification agent magnesium acetate.[52,58] In an article published in 1969, Baynes-Cope described his use of barium hydroxide in methanol for deacidification.[59] Two known problems exist with regard to this process: the deacidification solution is potentially more toxic to humans than other organic solvent-based solutions;[52] (pp. 27–8),[60] (p. 286) if the solution used is strong enough to deposit a buffer, the paper yellows.[48]

3.4 Mass Methods of Deacidification

Mass methods of deacidification are desperately needed because of the immensity of the problem of acidity of paper. A mass method is defined as one which simultaneously treats hundreds or thousands of whole books. Three such processes are currently in stages of development; one is a liquified gas process; two are vapor-phase processes.

In 1965, Smith began investigation of a low-unit-cost mass deacidification process for use on general collections materials of libraries. With Smith's process whole books are vacuum dried, impregnated with magnesium alkoxides, and flash dried. The chemistry of the method is accepted and the deacidification solution is used by conservators to deacidify single sheets of paper. An in-progress pilot project at the Public Archives of Canada is expected to treat at least 150 books per day.[61] (p. 149). In 1970, the Barrow Research Laboratory began exploratory work on a mass deacidification process. The result of this work is a process based on the impregnation of whole books with a mixture of morpholine vapor and water vapor. In 1977, the process underwent a trial run at the Virginia State Library in Richmond, Virginia. Walker reported that 250 books a day were successfully treated.[62] (p. 72). Circa 1974, the Preservation

Research and Testing Office of the Library of Congress began development of a mass deacidification process whereby books are vacuum dried and exposed to diethyl zinc vapor. The process is reported to have worked successfully on experimental runs treating four hundred books.[63] (pp. 81, 92).

The literature reviewed reflects two trends in the activity of science in library conservation during the period being studied. One trend is increased activity. One example is the increase in activity at the NBS beginning in the late sixties. Another example is the establishment of the Preservation Research and Testing Office of the Library of Congress. Another example is the number of patents awarded on deacidification and stabilization of paper. Prior to 1970, about one U.S. patent was awarded per decade; thereafter more than one a year was granted.[64] Another trend is increased effort to develop a mass deacidification method.

Neither the Preservation Research and Testing Office nor a mass deacidification system is a post-flood idea, and no grounds exist on which to attribute the increased activity at the NBS or the increased number of patents to the flood. Nevertheless, the salvage operation in Florence probably had an effect on the activity of science in conservation. Support for increased activity by scientists was in process prior to the flood. The salvage operation at Florence made conservators and librarians more aware of the need for and potential value of scientific investigation in library conservation, and the movement toward more support accelerated.

The salvage operation also affected the development of mass methods of deacidification. Librarians and conservators realized that deacidification by currently accepted methods would not make even a dent in the amount of material needing deacidification and, if a new approach was not developed, major portions of all library collections would be lost. The need for a mass method was recognized before the flood: one method was in the process of development. The salvage operation at Florence proved the feasibility of mass treatment, caused more conservators to accept the concept of mass treatment, and thus prompted additional investigations into the mass deacidification of whole books.

4. Physical Treatment

The emphasis of conservation work in Florence was physical treatment. Conservators from many countries met in Florence to develop ways to salvage the masses of flood damaged materials. They compared known methods, decided which were best, and either used or adapted the methods for application to the problems at hand. Many conservators active in Florence (Paul Banks, Christopher Clarkson, Don Etherington, Carolyn Horton, Peter Waters, Richard Young) are now active in the United States and are known to be using techniques proven in Florence. Thus the influence of the flood is anticipated to be especially strong in the area of physical treatment.

Today the basic techniques used in the treatment of library materials include washing, deacidification, sizing, mending, lamination, encapsulation, and binding. Some of these techniques, such as washing and sizing, are rarely mentioned in the literature. Other techniques, such as deacidification and lamination, are discussed frequently.

4.1 Binding

As shown above, standards have guided the binding of books valuable only for informational content. For the most part, these standards have determined the techniques used in this type of binding. These techniques include oversewing for regular volumes, and through-the-fold sewing, stab-sewing, side-sewing, and adhesive binding for exceptional volumes.[17] (pp. 71–5).

Due to the lack of standards for the binding of books of value as artifacts, the techniques used in the binding of these books are not as concisely expressed in the literature. For the purposes of discussion, this type of binding is referred to as conservation binding despite the inaccurate implication that the type of binding discussed above is not a conservation treatment.

Ideas of what constitutes a conservation binding emerged as a result of the flood. Most of the books damaged by the flood were in original bindings. Some of these bindings were in good condition before the flood, and others were in poor condition. In the process of treating the books in Florence, conservators observed this difference in condition and realized that some binding techniques which were assumed to be sound were actually damaging. This evidence caused conservators to reconsider techniques they employed and to adopt features which had proven non-damaging over time. As Waters explained:

> It was a great privilege even to see these flood-damaged books. . . We had an opportunity to see hundreds and hundreds of books in certain conditions and the most noticeable feature that came over was the damage that was already done before the flood happened. It is on this basis that I think we should rethink some of the things that we do in our work.[65] (pp. 13–14)

Prior to the flood, binding was considered in terms of designer/art binding, trade binding, or commercial library binding. After the flood, another category of binding developed, conservation binding. As Waters went on to say, "what I think we have to do is to try and find what I would like to call a conservation binding."[65] (p. 14). The ideas about what constitutes a conservation binding which have emerged deal with structural features which are non-damaging to the book-block. These ideas are based on techniques which were in practice before the flood, such as sewing all-along on raised cords or on tapes, utilizing original sewing holes, and incorporating barriers between certain adhesives and the book-block.[3,5,6,66–68]

4.2 Mending

The preferred conservation mending technique for materials of value as artifacts is the Japanese paper and paste method. The Japanese paper is water-torn to the shape of the tear or the missing area. This produces a repair with a soft, frayed edge rather than a hard, sharp one which acts as a breaking edge against which the object may fracture when flexed. Although this technique was mentioned in the pre-flood literature, it was not widely practiced before the flood.[9] (p. 261). The Japanese paper and paste method was used widely in the restoration work in Florence and represented a change from the usual practice of using Western papers and beveling both the edges of the mending paper and the edges of the missing area of the object to form a perfect fit.[69] (p. 53). The use of heat-set tissue for mending was also known but not widely practiced prior to the flood[1] (pp. 61–2); the technique was used in Florence, improved repeatedly, and is used frequently today. For non-artifact material, the use of pressure sensitive tape, of which many varieties exist, appears to have been prevalent both before and since the flood.

4.3 *Lamination and Polyester Film Encapsulation*

Numerous references to lamination appear in the literature, with cellulose acetate film and tissue lamination discussed most. The National Bureau of Standards developed lamination in the mid-thirties and Barrow derived his cellulose acetate and tissue lamination method from it in 1938. For years lamination was widely employed as the solution to the brittle paper problem. However, many laminated documents began to yellow and turn brittle. This deterioration has been attributed to a lack of deacidification, improper deacidification, inferior laminating materials, and to the heat and pressure applied to the document during the lamination process. The yellowing and embrittlement of many laminated documents, plus the fact that lamination is not readily reversible, have caused use of the process for materials of value as artifacts to be questioned.[69] (pp. 157–8),[3] (p. 203). This change in attitude was reflected in the literature around 1976 and does not appear to be related to the Florence flood.

Polyester film encapsulation was developed as an alternative to lamination.[70] (p. 8). Encapsulation is most suitable for unbound objects and "provides superior physical protection for fragile documents, can be accomplished without expensive treatment, is instantly reversible, is fully archival, and requires no heat or pressure which may damage the document."[71] (p. 168). The treatment has been tested and appears to be stable for the equivalent of a five hundred year period.[69] (p. 158).

4.4 *Restoration Office of the Library of Congress*

When the impact of the Florence flood on the physical treatment of library materials is examined, one particular library facility for physical treatment, the Restoration Office of the Library of Congress, should be considered. The work of the Restoration Office, which deals almost exclusively with materials of value as artifacts, is strongly influenced by the Florentine salvage operation. Since the Restoration Office serves as a model for other libraries, presumably what is done at LC will eventually be practiced throughout the United States. Hence influences of the flood on the Restoration Office will be passed on to other facilities which treat books of value as artifacts.

The term "Anglo-Florentines" is sometimes used to refer to the British book conservators who went to Florence to assist in the salvage operation. Three Anglo-Florentines became staff members of the Restoration Office. The first to be hired was Peter Waters.

Waters' employment by LC, first as a consultant and later as Restoration Officer, is believed to be a result of his contribution to the salvage operation at Florence. He had already established his reputation as a skilled book restorer through his partnership with Roger Powell. However, it was his participation in the organization and management of the salvage operation at the Biblioteca Nazionale Centrale di Firenze which demonstrated his ability to deal with large numbers of items on a mass basis, an ability needed at LC. The Anglo-Florentines subsequently employed were Don Etherington and Christopher Clarkson (Clarkson recently joined the staff of the Walters Art Gallery, Baltimore, Maryland; Waters and Etherington are still at the Library of Congress). Their experience in Florence and association with Waters is believed to have been significant in their affiliation with LC.

The salvage operation in Florence is influential in the operation of the Restoration Office in two important ways. One way is in design of the work areas of the Restoration Office; Waters based the layout of the workshop and the choice of equipment on experience gained while planning and working in the workshop at the Biblioteca Nazionale Centrale. The other way is in the techniques which have been used in the Restoration Office since its modernization in 1970. Many of the techniques now used at the Restoration Office are either those developed and used at Florence and introduced at LC by Waters, Etherington, and/or Clarkson or represent improvements of Florentine techniques. Further, as discussed previously, ideas of what constitutes a conservation binding emerged as a result of the Florentine experience. These ideas, developed in part by these three individuals, affect the specification of all binding done in the Restoration Office.

4.5 Regional Centers

Most libraries have funds for the physical treatment of their non-artifact books, that is, for commercial library binding, allocated in their annual budgets. However, the physical treatment of books of value as artifacts is much more expensive and well beyond the budgets of most libraries. Librarians are attempting to augment their funds for the treatment of artifactual material through the establishment of cooperative, non-profit regional centers. The current concept of a regional center for the physical treatment of library materials was introduced in the late sixties by George Cunha. In 1971, he and co-author Dorothy Cunha wrote:

> . . . For a great many years to come, even in the most carefully preserved libraries, books and artifacts on paper will require expert attention. This service is costly, whether it is done on the premises or outside. A cooperative approach to conservation would provide the special skills and equipment required at minimum cost. By such an effort, regionally associated libraries could accomplish jointly what most are unable to do by themselves.[15] (v. 1; p. 222)

Cunha established the New England Document Conservation Center as a non-profit institution supported and directed by librarians from several New England state agencies. The Center was funded originally by contributions and grants, with the CLR granting over seventy thousand dollars. The Inter-museum Conservation Association, a regional center serving museums, acted as a model for planning the Center. According to the brochure of the NEDCC, "the purpose of the Center is to administer and supervise a workshop with the necessary facilities and staff to restore, preserve and maintain the physical condition of books, prints, maps, broadsides, manuscripts and similar documentary materials of historic, archival or cultural interest."[72] Under certain circumstances the Center may also test materials and equipment, consult, and publish technical information. At present the only comparable regional center for library conservation is the Ohio Conservation Consortium which is on a much smaller scale than the NEDCC. The Consortium is sponsored and

housed by the Ohio Historical Society. It was established on a casual basis to provide conservation and educational services to its members.[73] (p. 128).

Even though the number of regional centers for the physical treatment of library materials is not increasing rapidly, the literature indicates that enthusiasm is. The description of the National Preservation Program for Libraries, a plan for the conservation of library materials on a national level, stated that "one of the most effective and productive national conservation programs the Library of Congress could undertake would be the establishment of one or more regional conservation centers."[74] (pp. 5–6). The Library and Archives Commitee of the NCAC stated that "there is much to commend regional or cooperative centers" and went on to mention cost reduction, possible raising of standards, dissemination of information, and training.[14] (p. 12). Banks said that "because of the increasing cost and complexity of conservation it seems almost certain that regional centers will be an increasingly important means of providing service."[3] (p. 219).

4.6 Mass Preservation Methods

Although cooperative, non-profit regional centers may be a more economical approach to physical treatment of materials of value as artifacts than in-house facilities or private conservation operations, the price of treatment is still high, especially when the quantity of materials requiring treatment is considered. The only possible solution lies in development of low-unit-cost mass preservation methods for the treatment of both artifact and non-artifact materials. As Poole explained:

> Where thousands, hundreds of thousands, and even millions of items must be dealt with, treatment on an item-by-item basis is economically unsound and practically impossible. The truth is that those who control library-archive budgets will not accept the cost of item-by-item conservation wherever mass treatment methods are technically possible. Thus, what today's librarian hopes for and today's conservator is actively seeking are methods by which deteriorating materials can be effectively treated in large numbers.[75] (pp. 150–51)

The restoration operations in Florence brought to people's attention the fact that quality conservation treatment can be carried out on a mass production basis; large numbers of books were washed, deacidified, mended and rebound to conservation standards. The next logical step is to further mechanize these conservation treatments, and others as well, so that they can be applied to entire collections of library materials. One example of such efforts is the current investigations of mass deacidification treatments discussed above. Another is development of the leafcasting technique for mending which utilizes a machine for the filling of lacunae in paper with paper pulp; the technique is superior to and more rapid than hand methods.

4.7 Treatment of Water-Damaged Materials

In 1970, Waters remarked:

> Those of us who, in one way or another, have been associated with the rescue and restoration operations of books and archives in Florence since the flood of 1966, would agree that the conservation world was completely unprepared for such a disaster, for there were few universally-established guidelines to follow.
>
> Most institutions which have suffered disasters must have kept records of their restoration programmes but nothing has been published in the international journals on this problem of large-scale treatment. My own researches into fire and water damage since the flood, have in fact revealed a distressing lack of information on the practical treatment given to damaged books[1] (pp. 60–61)

About twelve years earlier Amber et al. had made a search of the literature to see what was available on water-damaged materials and also found that very little existed.[76] (p. 5). The references in the pre-flood literature which exist do not serve as guidelines.[76–79] Although they tell the reader what to do in an emergency, the information is not given in sufficient detail or in the proper order to guide the activity of the librarian who is faced with masses of water-soaked materials. Also, these references deal mostly with documents; those which discuss the treatment of books, discuss exclusively the treatment of small numbers of books because, according to Minogue, no satisfactory method of treating large numbers of wet volumes was known.[79] (pp. 23–4).

After the flood, two changes in the literature occurred: the number of references to the treatment of water-damaged materials increased;[17,80–84] emphasis shifted from methods of handling small numbers of objects to methods of handling large numbers. One work produced which serves as a valuable set of guidelines is Waters' *Procedures for Salvage of Water-Damaged Library Materials*. This document, based on Waters' experience in Florence and with salvage operations in this country and on research conducted by the Preservation Research and Testing Office at LC, is intended to assist individuals both in preparing for disaster and in salvaging water-damaged library materials. Waters stated that "the procedures suggested . . . are designed to save a maximum amount of material with a minimum amount of restoration and replacement.[79] (p. iii).

More research into various methods of recovering water-soaked materials

was conducted after the flood than before the flood. The only reference to such research in the literature reviewed which dates from before the flood is to a study conducted in 1937 by the Research Department of the LBI which indicated that the most important factor in the salvage operation is individual careful handling before, during, and after drying.[85] After the flood, however, references to research are numerous. The publications deal almost exclusively with mass drying methods. Cunha attributed this change in activity to the Florence flood and to other floods which followed:

> Experiences at Florence and equally serious waterdamage disasters since . . . did initiate investigations of methods for the mass drying of books that hopefully will result ultimately in procedures that will be technically sound, aesthetically satisfactory, and economically feasible.[86] (p. 95)

The investigations to which Cunha refers include research conducted by the Preservation Research and Testing Office of the Library of Congress on the "mechanisms and safety parameters" of all known drying techniques; the purpose of this research was to find a drying method which is economical and which causes minimal damage to cellulose and related materials.[70] (pp. 7–8),[86] (p. 96). These investigations also include research on the Corning Museum flood damaged library materials to determine the most economical and successful method for drying the thousands of soaked books which were frozen shortly after the flood in Corning, New York.

As a result of these investigations, the freeze/thaw/vacuum drying process has been generally accepted as the most suitable for large numbers of water-soaked books. Wet materials are frozen and stored at low temperature (−20°F) until further treatment can be planned. They are then vacuum-dried, a technique which causes "the water to sublime, i.e. pass from the frozen to the vapor phase without going through the liquid phase. Under these conditions feathering of inks is negligible. Further, freeze drying reduces stains and reduces or eliminates the odor caused by smoke."[84] (p. 6).

In the course of discussing physical treatment of library materials, Waters explained that as a result of the circumstances in Florence:

> . . . The traditional concepts and practices of book preservation have been subjected to reassessment and new criteria. In effect, a revolution is in progress.[1] (p. 71)

Many changes have occurred in physical treatment since the Florence flood. Some are directly attributable to the flood and others are not. Sufficient time has not yet passed since the flood to verify that Waters' "revolution" is in progress. However, if mass physical treatment techniques are developed and applied, the result will be the revolution which Waters anticipates.

5. Conclusion

This study examined the assertion by Banks, Cunha, and Waters that the Florence flood is a turning point, that it marks a change in the direction of the development of the field of library conservation in the United States. In general, the findings of the study indicate that the Florence flood accelerated the development of library conservation in directions in which it was already moving or had no effect on the development. The flood was found to mark a turning point in the physical treatment of books of value as cultural artifacts.

The principles of library conservation followed today were mentioned in the literature before the flood but were discussed, critically evaluated, and applied more often after the flood. This is because the salvage operation raised the level of awareness of the value of conservation and of what constitutes certain conservation treatments. The only specifications which are applicable to library conservation and which qualify as standards are those guiding the binding of material valuable for informational content only. These specifications existed or were in the process of development before the flood.

Two trends in the activity of science in conservation are apparent: increased activity and increased interest in development of a mass deacidification method. The salvage operation raised the level of awareness of and support for scientific investigation in library conservation. The salvage operation demonstrated the feasibility of mass treatment, caused more people to accept mass treatment, and thus prompted additional investigations into mass deacidification.

Establishment of regional centers for physical treatment is a result of the flood to the extent that the salvage operation increased awareness of the benefits of the physical treatment of library materials; librarians became more interested in having materials from their collections treated and saw regional centers as a means of obtaining this treatment.

The salvage operation had no effect on certain changes which occurred in the field. For example, the change in attitude regarding the use of lamination for materials of value as cultural artifacts does not appear to be related to the salvage operation. The technique of encapsulation was not developed in response to a need created or made apparent by the salvage operation but rather as an alternative to lamination.

The salvage operation marked a turning point or change in direction for certain physical treatments. After the flood, investigations into methods of treatment of large numbers of water-damaged materials were conducted for the first time in the United States, and one method – the freeze/thaw/vacuum drying process – was demonstrated as suitable and is now generally accepted.

This development cannot be attributed solely to the Florence flood. Although the Florentine salvage operation pointed out the need for the development of a method of treating large numbers of objects, it was not until several libraries in the United States suffered major losses from water damage that investigations were conducted.

The Florentine salvage operation appears to be solely responsible for the rapidity of the change in mending techniques considered acceptable for materials of value as artifacts. The use of Japanese paper and paste was mentioned in the pre-flood literature but was not widely practiced before the flood; this technique was used widely in Florence and is now the preferred technique for mending materials of value as artifacts. The use of heat-set tissue was also known but not widely practiced prior to the flood. It was used in Florence, improved repeatedly, and is now used for materials of value as artifacts.

Ideas of what constitutes a conservation binding emerged as a result of the Florence flood. Although these ideas are based on techniques which were in practice prior to the flood, these ideas were crystallized as a consequence of the flood.

The operation of the Restoration Office of the Library of Congress can be considered a new development or a change in direction. Although the establishment of the Restoration Office was in process prior to the flood, its organization was strongly influenced by the Florentine salvage operation; the Restoration Office is the only facility of its scope, is pre-eminent in its influence, and is believed different from what it would have been had the flood not occurred.

This study indicates that the only area of library conservation in which documented changes in direction occurred as a result of the Florentine salvage operation is the physical treatment of materials of value as artifacts. The definition of the term "library conservation" as used by Banks, Cunha, and Waters in their discussions of the impact of the Florence flood is ambiguous. If they limited the definition of library conservation to the physical treatment of materials of value as cultural artifacts, their assertion that the flood marked a turning point is supported by the literature.

In summary, most of the changes in library conservation which occurred after the flood were in motion prior to the flood. The salvage operation and the publicity it received raised the level of public support for the conservation of library materials. Conservation was glamorized and popularized. The flood occurred during a period of economic prosperity and the new popularity of library conservation was reinforced by the availability of funds for it. The net result was that the Florentine salvage operation, rather than changing the direction of the field, accelerated the development of conservation in directions in which it was already moving.

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7. APPENDICES

7.1 APPENDIX 1

REPORTS AND PAPERS ISSUED BY THE PRESERVATION OFFICE, LIBRARY OF CONGRESS*

Preservation Leaflets.

Selected References in the Literature of Conservation. February, 1975, 4 p.
Environmental Protection of Books and Related Materials. February, 1975, 4 p.
Preserving Leather Bookbindings. February, 1975, 4 p.
Marking Manuscripts. February, 1977, 4 p.
The Physical Protection of Brittle and Deteriorating Documents by Polyester Encasement, [Working Draft]. October 15, 1975, 8 p.
Preserving Newspapers and Newspaper Type Materials, [Working Draft]. Revised June 1976, 9 p.

Conservation Workshop Notes on Evolving Procedures. Series 100.

Making a Phased Preservation Box, [Working Draft]. August, 1976, 12 p.
– Supplement [no date]. 5 p.
Making a Lip-On-Casing Box, [Working Draft]. August, 1976, 12 p.
Making a Portfolio (Stiffened Flaps, One-Piece Covering), [Working Draft]. August, 1976, 6 p.

Conservation Workshop Notes on Evolving Procedures. Series 200.

Collation Practice, [Working Draft]. August 1976, 9 p.

Conservation Workshop Notes on Evolving Procedures. Series 300.

Heat-Set Tissue Preparation and Application, [Working Draft]. May 1977, 8 p.
Polyester Film Encapsulation, [Working Draft]. August 1977, 11 p.
Making a Polyester Envelope, [no date]. 5 p.
Polyester Film Encasement for a Folded Item, [no date]. 5 p.

* Derived from the list compiled by Richard D. Smith for course no. 348, Conservation of Library Materials, Graduate Library School, University of Chicago.

Conservation Workshop Notes on Evolving Procedures. Series 400.

Rice Starch Paste (Stock Paste for Covering), [Working Draft], July 1977, 2 p.
Wheat Starch Paste (Stock Paste for Mending, Lining and Hinging Works of Art on Paper), [Working Draft], July, 1977, 3 p.
Cellulose Ether Solution for Long Fiber Mending and Wash/Sizing of Single Sheets, [Working Draft], August 1976, 2 p.

Conservation Workshop Notes on Evolving Procedures. Series 500.

The Deacidification and Alkalization of Documents with Magnesium Bicarbonate, [Working Draft], July 1977, 15 p.
Deacidification – Methyl Magnesium Carbonate Non-Aqueous Treatment, [Working Draft], July, 1977, 12 p.

Conservation Workshop Notes on Evolving Procedures. Series 600.

Display Cradles for Books: Board Construction, [Working Draft], July 1977, 27 p.

Pre-Prints

Hey, Margaret and Peter Waters: Heat-Set Tissue. May 27, 1977, 19 p.
Brown, Margaret *et al.*: Design and Construction of Boxes for the Protection of Rare Books. [no date]. 186 p.

L. C. Publications on Conservation of Library Materials.

Waters, Peter. Procedures for Salvage of Water-Damaged Library Materials. 1975, 30 p.

7.2 APPENDIX 2

REPORTS ISSUED BY THE NATIONAL BUREAU OF STANDARDS*

Accelerated Aging of Commercial Papers in Dry Air, Compared with Natural Aging. National Bureau of Standards Paper Research Report 73–155. 30 March 1973.
Development of Specifications for Archival Record Materials. National Bureau of Standards Paper Research Reports 10–152; 31 December 1969. 10–466; 30 June 1971. 10–517; 31 December 1970. 10–696; 21 January 1972. 10–887; 30 June 1972. 10–979; 12 January 1973. 73–249; 30 July 1973. 74–501; 23 May 1974.
Development of Specifications for Bond and Ledger Papers for Permanent Records. 10–844. 1 May 1972.
Development of Specifications for File Folders for Storage of Permanent Records. National Bureau of Standards Paper Research Report 10–843. 1 May 1972.

* Compiled by William K. Wilson, formerly Chief, Paper Evaluation Section, National Bureau of Standards, Washington, D.C., 20234 and presently with the Preservation Services Division, National Archives and Records Service, Washington, D.C., 20408.

Evaluation of Archival Stability of Copies from Representative Office Copy. National Bureau of Standards Paper Research Report 74–498 (R). 30 April 1974.

Evaluation of Condition of Manifold Papers in File. National Bureau of Standards Paper Research Report 10–429. 7 June 1971.

Flynn, J. H. and Smith, L. E. Comparative pH measurements on papers by water extraction and glass electrode spot tests. Tappi. 44 (1961): 223.

Flynn, J. H., Wilson, W. K., and Morrow, W. L. Degradation of Cellulose in a Vacuum with Ultraviolet Light. Journal of Research of the National Bureau of Standards 60 (1958): 229.

Graminske, E. L.: The Stress-Strain Behavior of Accelerated and Naturally Aged Papers. Tappi 53 (1970): 406.

Hebert, R. L., Tyron, Max, and Wilson, W. K.: Differential Thermal Analysis of Some Papers and Carbohydrate Materials. Tappi 52 (1969): 1183.

Parks, E. J. Thermal Analysis of Modified Cellulose. Tappi 54 (1971): 537.

Rasch, R. H. and Schribner, B. W. Comparison of Natural Aging of Paper with Accelerated Aging by Heating. Journal of Research of the National Bureau of Standards 11 (1933): 727.

A Source of Error in Paper Extract pH Determinations: Contact between Paper and Reference Electrode. National Bureau of Standards Paper Research Report 75–915. 31 January 1976.

Toner, S. D. and Plitt, K. F. Spectrophotofluorometric Studies of Degraded Cotton Cellulose. Tappi 45 (1962): 681.

Wilson, W. K. and Forshee, B. W. Preservation of Documents by Lamination. Washington, D. C.: National Bureau of Standards, 1959.

Wilson, W. K., Harvey, J. L., Mandel, John and Worksman, Thelma. Accelerated Aging of Record Papers Compared with Normal Aging. Tappi 38 (1955): 543.

Wilson, W. K. and Hebert, R. L. Evaluation of the Stability of Manifold Papers. Tappi 55 (1972): 1103.

Wilson, W. K. and Hebert, R. L. Evaluation of the Stability of Record Papers. Tappi 52 (1969): 1523.

Wilson, W. K. and Parks, E. J. Comparison of Accelerated Aging of Book Papers in 1937 with 36 Years Natural Aging. Washington, D.C.: National Bureau of Standards, 1974.

7.3 Appendix 3

ACRONYMS

American Library Association	ALA
Book Manufacturers' Institute	BMI
Council on Library Resources, Inc.	CLR
Cyclohexylamine Carbonate	CHC
Library Binding Institute	LBI
Library of Congress	LC
National Bureau of Standards	NBS
National Conservation Advisory Council	NCAC
New England Document Conservation Center	NEDCC
Vapor Phase Deacidification	VPD

8. Summaries

The Florence flood of November 4, 1966 is asserted by prominent conservators, namely Paul N. Banks, George M. Cunha, and Peter Waters, to be a turning point in the development of conservation in the United States. Indeed library conservation has changed in the years since the flood, but the question of whether the flood represents a turning point or change in direction has not been examined. This study reviews the literature of library conservation written prior to and after the flood to determine the nature of the changes and the impact of the flood on the development of conservation.

The literature examined is limited to publications issued between 1956 and 1976, the ten years prior to the flood and the ten years after the flood. The ten-year periods were chosen because a decade is judged as sufficient time for changes to become evident and not so much time as to be unmanageable. Also, this particular twenty year period can be considered to represent the real-life-time of the field since very little was going on in the field prior to 1956. However, the scope of the study is not rigidly restricted to the twenty year period; when a work of significance was found which lies outside the allotted period, it was included.

The definition of "library conservation" used in this study is limited to books. Microform, maps, manuscripts and other forms of library materials are, for the most part, excluded. The definition includes (1) standards for and philosophy of physical treatment, (2) scientific investigation in deterioration and preservation, and (3) techniques of physical treatment. Both the preservation of books of value for informational content only and the preservation of books of value as cultural artifacts are included.

In general, the findings of the study indicate that the Florence flood accelerated the development of library conservation in directions in which it was already moving or had no effect on the development. The flood was found to mark a turning point in the physical treatment of books of value as cultural artifacts.

The principles of library conservation followed today were mentioned in the literature before the flood but were discussed, critically evaluated and applied more often after the flood. This is because the salvage operation raised the level of awareness of the value of conservation and of what constitutes certain conservation treatments. The only specifications which are applicable to library conservation and which qualify as standards are those guiding the binding of material valuable for informational content only. These specifications existed or were in the process of development before the flood.

Two trends in the activity of science in conservation are apparent: increased activity and increased interest in development of a mass deacidification method. The salvage operation raised the level of awareness of and support for scientific investigation in library conservation. The salvage operation demonstrated the feasibility of mass treatment, caused more people to accept mass treatment, and thus prompted additional investigations into mass deacidification.

Establishment of regional centers for physical treatment is a result of the flood to the extent that the salvage operation increased awareness of the benefits of physical treatment of library materials; librarians became more interested in having materials from their collections treated and saw regional centers as a means of obtaining this treatment.

The salvage operation had no effect on certain changes which occurred in the field. For example, the change in attitude regarding the use of lamination for materials of value as cultural artifacts does not appear to be related to the salvage operation. The technique of encapsulation was not developed in response to a need created or made apparent by the salvage operation but rather as an alternative to lamination.

The salvage operation marked a turning point or change in direction for certain physical treatments. After the flood, investigations into methods of treatment of large numbers of water-damaged materials were conducted for the first time in the United States, and one method – the freeze/thaw/vacuum drying process – was demonstrated as suitable and is now generally accepted. This development cannot be attributed solely to the Florence flood. Although the Florentine salvage operation pointed out the need for development of a method of treating large numbers of objects, it was not until several libraries in the United States suffered major losses from water damage that investigations were conducted.

The Florentine salvage operation appears to be solely responsible for the rapidity of the change in mending techniques considered acceptable for materials of value as artifacts. The use of Japanese paper and paste was mentioned in the pre-flood literature but was not widely practiced before the flood; this technique was used widely in Florence and is now the preferred technique for mending materials of value as artifacts. The use of heat-set tissue was also known but not widely practiced prior to the flood. It was used in Florence, improved repeatedly, and is now used for materials of value as artifacts.

Ideas of what constitutes conservation binding emerged as a result of the Florence flood. Although these ideas are based on techniques which were in practice prior to the flood, these ideas were crystallized as a consequence of the flood.

The operation of the Restoration Office of the Library of Congress can be considered a new development or change in direction. Although the establishment of the Restoration Office was in process prior to the flood, its organization was strongly influenced by the Florentine salvage operation; the Restoration Office is the only facility of its scope, is pre-eminent in its influence, and is believed different from what it would have been had the flood not occurred.

This study indicates that the only area of library conservation in which documented changes in direction occurred as a result of the Florentine salvage operation is the physical treatment of materials of value as artifacts. The definition of the term "library conservation" as used by Banks, Cunha, and Waters in their discussions of the impact of the Florence flood is ambiguous. If they limited the definition of library conservation to the physical treatment of materials of value as cultural artifacts, their assertion that the flood marked a turning point is supported by the literature.

In summary, most of the changes in library conservation which occurred after the flood were in motion prior to the flood. The salvage operation and the publicity it received raised the level of public support for the conservation of library materials. Conservation was glamorized and popularized. The flood occurred during a period of economic prosperity and the new popularity of library conservation was reinforced by the availability of funds for it. The net result was that the Florentine salvage operation, rather than changing the direction of the field, accelerated the development of conservation in directions in which it was already moving.

L'inondation que la ville de Florence a subi le 4 novembre 1966 représente, conformément aux assertions des conservateurs éminents de bibliothèque tels que Paul N. Banks, George M. Cunha et Peter Waters, un tournant dans le développements des techniques de conservation aux Etats-Unis. Les méthodes de conservation appliquées aux bibliothèques ont effectivement changé depuis l'inondation sus-citée, mais le problème consistant à savoir si l'inondation représente un tournant ou un changement de direction n'a pas été examiné. Cette étude se propose de passer en revue les oeuvres portant sur la conservation des bibliothèques écrites avant et après l'inondation afin de

déterminer la nature des changements apparus et l'impact de cette inondation sur le développement des techniques de conservation aux Etats-Unis.

Les oeuvres examinées se limiteront aux publications parues entre 1956 et 1976, soit une décennie avant et une décennie après l'inondation. Des périodes de dix ans ont été retenues du fait qu'une décennie représente d'une part un intervalle de tempts suffisant rendant tout changement apparent et d'autre part un laps de temps tel que le traitement de l'ensemble des données s'avère possible. Il convient de noter aussi que cette période particulière de vingt ans peut être considèrée comme représentative de la durée d'existence effective de ce domaine du fait de l'ampleur réduite des activités avant l'année 1956. Toutefois, le cadre de cette étude n'est pas limité strictement à la période mentionnée de vingt ans; des travaux importants découverts et situés en dehors de la période assignée ont été inclus dans le cadre de cette étude.

La dfinition du terme "conservation de collections de livres" utilisé dans cette étude est limitée aux livres seulement. Les formats type micro, les cartes, les manuscrits et toutes autres types de documents de bibliothèque ont, pour la plupart, été exclus. La définition inclut: 1) les standards et l'approche conceptuel des traitements physiques appliqués, 2) les investigations scientifiques traitant de la détérioration et de la préservation, 3) les techniques de traitement d'ordre physique. La définition s'applique á la conservation de livres d'une valeur exclusivement informative et de livres représentant une valeur d'ordre culturel.

En général, les conclusions découlant de cette étude indiquent que l'inondation qu'a connu Florence a accéléré le développement de la conservation de collections de livres dans des directions tracées au préalable sans exercer d'influence sur le degré de développement proprement dit.

L'inondation s'est avérée représenter un tournant au niveau du traitement physique des livres de valeur considérés comme objects à caractère culturel.

Les principes de la conservation de collections de livres adoptés à l'heure actuelle avaient été mentionnés dans divers documents avant l'inondation, mais ils ont été discutés, soumis à une évaluation d'ordre critique et appliqués plus fréquemment après les inondations sus-citées.

Durant cette décennie, les opérations de sauvegarde ont accru le niveau de conscience de la valeur des opérations de conservation et des éléments constitutifs s'appliquant aux traitements de conservation efficace. Les seules spécifications s'appliquant à la conservation des collections de livres qui ont reçu une qualification s'assimulant à des standards, sont celles servant de guide de reliure de documents présentant exclusivement une valeur d'ordre informatif. Ces spécifications existaient ou étaient en voie de développement avant l'époque de l'inondation.

Deux tendances se dessinent au niveau des activités scientifiques de conservation, à savoir un accroissement de ces activités et un intérêt accru dans le développement des méthodes de désacidification en masse. Les opérations de sauvetage ont accru le niveau de conscience et de soutien à l'égard d'investigations scientifiques s'appliquant à la conservation des collections de livres. Les opérations de sauvetage ont fait la preuve de la fiabilité des traitements en masse, tout en accroissant le degré d'acceptation de ces traitements et tout en accélérant le nombre d'investigations supplémentaires portant sur la technique de désacidification en masse.

L'éstablissement de centres régionaux de traitement d'ordre physique est une conséquence de l'inondation du fait que l'opération de sauvetage-sauvegarde a accru le degré de conscience des avantages offerts par le traitement physique des documents de bibliothèque. Les bibliothécaires ont fait preuve d'un intérêt accru pour le traitement des documents de leurs collections et ils on entrevu l'intérêt offert, au niveau du traitement, par les centres régionaux.

L'opération de sauvetage entreprise à Florence n'a pas eu d'effet sur certains changements apparus dans ce domaine d'activités. Par example, le changement d'attitude à l'égard de l'utilisation du traitement de feuilletage appliqué à des documents offrant une valeur d'objects culturels ne semble pas corroborer avec la période de l'opération de sauvetage. La technique d'enrobage n'a pas été mise au point en réponse à un besoin crée ou rendu apparent lors de l'opération de sauvetage, mais plutôt à titre de solution alternative au feuilletage.

L'opération de sauvetage a marqué un tournant ou un changement de direction de certains traitements d'ordre physique. Après l'inondation des recherches portant sur les méthodes de traitement de quantités importantes de documents endommagés au contact de l'eau ont pu être menées pour la première fois aux Etats-Unis. Une méthode nommée processus de congélation/décongélation/séchage sous vide s'est avérée applicable et est généralement acceptée à l'heure actuelle. Les progrès accomplis ne peuvent pas être attribués seulement aux inondations que Florence a connues. Bien que l'opération de sauvetage-sauvegarde entreprise à Florence ait mis l'accent sur la nécessité d'une mise au point d'une méthode de traitement d'une quantité importante d'objects, les recherches n'ont été entreprises qu'après que de nombreuses bibliothèques aux Etats-Unis aient souffert de dégâts et de pertes importants occasionnés par l'eau.

L'opération de sauvetage effectuée à Florence paraît n'avoir joué rôle qu'au niveau de la rapidité d'évolution des techniques de restauration jugées acceptables pour des matériaux présentant une valeur d'objets d'art. L'utilisation de papier et de pâte japonais avait été mentionnée dans les documents précédant l'inondation de Florence sans avoir connu une extension importante avant l'inondation. Cette technique a été utilisée sur une grande échelle à Florence et représente la technique préférée lors de la restauration de matériaux à caractère d'objets d'art. L'utilisation de tissus appliqués à chaud était également connue mais peu pratiquée avant les inondations en question. Cette technique a été utilisée à Florence, améliorée à plusieurs reprises et elle est appliquée à l'heure actuelle à des matériaux présentant une valeur d'objets élaborés.

Les idées constitutives de la technique de conservation par reliure ont pris naissance à la suite des inondations de Florence. Bien que ces idées aient été basées sur des techniques appliquées antérieurement à l'inondation, elles ont été concrétisées conséquemment à ce cataclysme.

L'opération entreprise par le Bureau de Restauration de la Bibliothèque du Congrès peut être considérée comme un développement nouveau ou un changement de direction. Bien que la fondation de Bureau de Restauration ait été antérieure à l'inondation, son organisation a été fortement influencée par les opérations de sauvetage entreprises à Florence. Le Bureau de Restauration est le seul organe d'une telle ampleur, présentant une influence prééminente dont l'évolution – estime-t-on par ailleurs – a été différente du fait de l'inondation de Florence.

Ces travaux indiquent que le seul domaine de la conservation de collections de livres dans lequel des changements prouvés de direction se soient produits du fait de l'opération de sauvetage de Florence, s'applique au traitement physique des matériaux représentant une valeur d'ordre culturel. La définition du terme "conservation de collections de livres" utilisé par Banks, Cunha et Waters lors des discussions concernant l'impact produit par les inondations de Florence s'avère être ambigue. Dans la mesure où la définition "conservation de collections de livres" est limitée au traitement physique de matériaux présentant une valeur culturelle, l'assertion consistant à soutenir que l'inondation a représenté un tournant est effectivement soutenue par les documents publiés.

En résumé, la majorité des changements apparus au niveau de la conservation des collections de livres et survenus après l'inondation, avait fait l'objet d'une progression antérieurement à l'inondation. L'opération de sauvetage et la publicité qu'elle a reçue a conduit à un accroissement du niveau des soutiens financiers publiés à la conservation des matériaux de bibliothèque. En fait, la conservation a exercé une fascination tout en devenant populaire. L'inondation de Florence est survenue durant une période de prospérité économique et la popularité nouvelle qu'a connu la conservation de collections de livres a été renforcée en raison de l'existence des fonds disponibles à cet effet. L'opération de sauvetage entreprise à Florence a conduit à un résultat net consistant, au lieu de modifier les directions prises par ce domaine d'activités, à accélérer le développement de la conservation dans des directions adoptées antérieurement au cataclysme.

Die Überschwemmung von Florenz vom 4. November 1966 wird von den bekannten Bibliotheks-Restauratoren Paul N. Banks, George M. Cunha und Peter Waters als ein Wendepunkt in der Entwicklung der Konservierung in den Vereinigten Staaten bezeichnet. Die Bibliotheks-Konservierung hat sich in den Jahren nach der Überschwemmung verändert, die Frage jedoch, ob die Überschwemmung einen Wendepunkt darstellt, ist nicht untersucht worden. Die vorliegende Arbeit beleuchtet die Literatur über Bibliotheks-Konservierung, die vor und nach der Überschwemmung erschienen ist, um die Art der Veränderungen und den Enfluss der Überschwemmung auf die Entwicklung der Konservierung in den Vereinigten Staaten zu untersuchen.

Die Literatur, die bearbeitet worden ist, beschränkt sich auf die Veröffentlichungen, die von 1956 bis 1976 erschienen sind, also die 10 Jahre vor und nach der Überschwemmung. Die beiden 10-Jahres-Perioden wurden deshalb gewählt, weil wir 10 Jahre als einen Zeitraum betrachten, der lang genug ist, um Veränderungen sichtbar werden zu lassen, und doch nicht so lang, dass die Arbeit unüberschaubar wird. Ausserdem kann diese 20-Jahres-Periode als die wirkliche „Bestehensperiode" dieses Zweiges betrachtet werden, denn vor 1956 ereignete sich auf diesem Gebiet in Wirklichkeit nur wenig. Der Umfang dieses Studiums beschränkt sich jedoch nicht streng auf diesen Zeitraum von 20 Jahren. Bedeutende Werke, die ausserhalb dieser abgesteckten Periode erschienen sind, sind mit einbezogen worden.

Die Definition „Bibliotheks-Konservierung", die in diesem Studium verwendet wird, beschränkt sich auf Bücher. Mikrofilme, Mappen, Manuskripte und andere Formen von Bibliotheksmaterial werden im grossen und ganzen ausgeschlossen. Die Definition umfasst (1) Standards für und die Theorie der physikalischen Behandlung, (2) die wissenschaftliche Untersuchung der Verminderung der Eigenschaften und der Erhaltung sowie (3) die Verfahren der physikalischen Behandlung. Die Definition umfasst sowohl die Erhaltung von Büchern, die lediglich auf Grund ihres informatorischen Inhaltes von Wert sind, als auch die Erhaltung von Büchern, die wertvolle Kunstgegenstände darstellen.

In grossen Zügen deuten die Untersuchungen an, dass die Überschwemmung die Entwicklung der Bibliotheks-Konservierung in Richtungen beschleunigte, in die sie sich bereits bewegte, oder dass sie keine Auswirkung auf die Entwicklung hatte.

Es wurde festgestellt, dass die Überschwemmung einen Wendepunkt in der physikalischen Behandlung der Bücher darstellte, die als kulturelles Erbe von Wert sind.

Die Prinzipien der Bibliotheks-Konservierung, nach denen man heute arbeitet, werden in der Literatur vor der Überschwemmung bereits genannt, aber nach der Überschwemmung wurden sie häufiger diskutiert, kritisch ausgewertet und angewendet. Die Ursache dafür ist die, dass man sich durch die Rettungsaktion dessen bewusst wurde, wie bedeutungsvoll die Konservierung ist.

Die einzigen Spezifikationen, die in der Bibliotheks-Konservierung anwendbar sind und die sich als Standards ausweisen, sind die, die mit dem Einbinden von Material zusammenhängen, das nur informatorischen Wert hat. Bereits vor der Überschwemmung gab es diese Spezifikationen, bzw. diese befanden sich in Entwicklung.

In der Tätigkeit der Konservierungs-Wissenschaft werden zwei Tendenzen sichtbar: eine grössere Aktivität sowie wachsendes Interesse an der Entwicklung einer Massen-Entsäuerungs-Methode. Die Rettungsaktion führte dazu, dass man sich der Bedeutung der Bibliotheks-Konservierung besser bewusst wurde und dazu, dass die wissenschaftliche Forschung in der Bibliotheks-Konservierung auf einer breiteren Basis unterstützt wurde. Die Restaurierungsaktion beweis die Durchführbarkeit der Massenbehandlung, sie trug dazu bei, dass die Massenbehandlung grössere Anerkennung fand und so wurden weitere Forschungen in die Richtung der Massenentsäuerung geleitet.

Als ein Ergebnis der Katastrophe wurden regionale Zentren für die physikalische Behandlung eingerichtet, die Überschwemmung liess die Bedeutung der Vorteile einer physikalischen Behandlung von Bibliotheksmaterial deutlich werden. Das Interesse der Bibliothekare, Materialien aus ihren Sammlungen behandeln zu lassen, wuchs spürbar an, regionale Zentren, die diese Behandlung ausführen sollten, waren der Ausdruck dafür.

Die Rettungsaktion hatte keinen Einfluss auf bestimmte Veränderungen, die sich auf diesem Gebiet ergaben, zum Beispiel hat die Änderung der Einstellung in Bezug auf die Verwendung der Laminierung von Materialien, die kulturelles Erbe darstellen, nichts mit der Restaurierungsaktion zu tun. Das Verkapselungsverfahren wurde nicht als Antwort auf einsich zeigendes Problem auf Grund der Restaurierungsarbeiten entwickelt, sondern vielmehr als Alternative zu der Laminierung.

Die Restaurierungsaktion stellte einen Wendepunkt dar, bzw. sie veränderte die Richtung für bestimmte physikalische Behandlungsverfahren. Nach der Überschwemmung wurden in den Vereinigten Staaten zum ersten Mal die Behandlungsmethoden für eine Vielzahl von wassergeschädigten Materialen erforscht. Eine Methode, nähmlich der Gefrier-/Saug-/Vakuum-Trocken-Prozess, erwies sich als anwendbar und ist jetzt allgemein anerkannt. Die Entwicklung kann nicht allein auf die Überschwemmung von Florenz zurückgeführt werden. Die Restaurierungsaktion in Verbindung mit der Überschwemmung von Florenz zeigte zwar ganz klar die Bedeutung und die Wichtigkeit für die Entwicklung einer Methode, mit der eine Vielzahl von Objekten behandelt werden konnten, dennoch dauerte es bis zu dem Zeitpunkt, wo verschiedene Bibliotheken in den Vereinigten Staaten grosse Verluste auf Grund von Wässerschäden erlitten, bevor hier Forschungen angestellt wurden.

Es sieht so aus, als ist die Restaurierungsaktion von Florenz allein für die schnelle Veränderung der Restaurierungsmethoden verantwortlich, die für Materialien von kulturellem Wert anwendbar sind. Die Verwendung von japanischem Papier und Paste wurde in der Literatur, die vor der Überschwemmung erschienen ist, erwähnt, aber vor der Überschwemmung nur in unbedeutendem Umfang angewendet. Diese Technik wurde in Florenz bei der Restaurierung von kulturell wertvollen Materialien vorrangig verwendet und ist heute das Verfahren, das bei der Restaurierung von kulturell wertvollem Material bevorzugt wird. Die Anwendung von heisstrocknendem Stoff war auch bereits vor der Überschwemmung bekannt, wurde aber kaum in der Praxis verwendet. Es wurde in Florenz verwendet, schnell verbessert und wird heute für Materialien verwendet, die als Kunstgegenstände von Wert sind.

Die Gedanken, die das Konservierungs-Einbinden betreffen, waren ein Ergebnis der Überschwemmung von Florenz. Obwohl diese Gedanken auf Verfahren beruhen, die vor der Überschwemmung praktiziert worden sind, haben sich diese Gedanken als eine Konsequenz der Überschwemmung herauskristallisiert.

Die Arbeitsweise des Restoration Office of the Library of Congress kann els eine neue Entwicklung oder als eine Richtungsänderung angesehen werden. Obwohl die Etablierung des Restoration Office vor der ±Uberschwemmung in Gang war, wurde dessen Organisation von der Restaurierungsarbeit in Florenz stark beeinflusst, man nimmt unbedingt an, dass das Office anders aussehen würde, wenn die Überschwemmung nicht stattgefunden hätte.

Die Untersuchung zeigt, dass das einzige Gebiet der Bibliotheks-Konservierung, das bewiesene Veränderungen auf Grund der Restaurierungsarbeiten von Florenz aufweist, die physikalische Behandlung von Materialien ist, die kulturellen Wert haben. Die Definition des Begriffes „Bibliotheks-Konservierung", wie er von Banks, Cunha und Waters in ihren Diskussionen des Einflusses der Überschwemmung von Florenz verwendet wird, ist verschwommen. Wenn sie die Begriffsdefinierung der Bibliotheks-Konservierung auf die physikalische Behandlung von Materialien, die kulturellen Wert haben, eingeschränkt hätten, dann wäre ihre Behauptung richtig, dass die Überschwemmung einen Wendepunkt darstellt, das beweist die Literatur.

Zusammenfassend kann gesagt werden, dass die Veränderungen in der Bibliotheks-Konservierung, die nach der Überschwemmung sichtbar wurden, bereits vor der Überschwemmung im Gange waren. Die Restaurierungsarbeiten und die Publicity, die ihnen zuteil wurden, erhöhten das Niveau der öffentlichen Unterstützung der Konservierung von Bibliotheks-Materialien. Konservierung wurde populär. Die Überschwemmung ereignete sich in einer Periode des ökonomischen Wohlstandes und die neue Popularität, die die Bibliotheks-Konservierung errungen hatte, wurde durch die zur Verfügung gestellten Fonds unterstützt. Das hauptsächliche Ergebnis der Restaurierungs-Arbeiten von Florenz bestand nicht so sehr darin, dass hier Richtungsänderungen auf diesem Gebiet vorgenommen wurden, sondern vielmehr darin, dass die Entwicklung der Konservierung in Richtungen beschleunigt wurde, in die sie sich bereits vor der Überschwemmung bewegt hatte.

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An Analysis of the Aging of Paper:

Possible Reactions and their Effects on Measurable Properties*

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Contents

1. Introduction

The permanence of paper and laboratory aging have been discussed extensively in the literature. Pertinent articles, including reviews, have been authored by Spinner,[1] Stübchen-Kirchner,[2] Niemo,[3] Browning and Wink,[4] Luner,[5] Millett,[6] Kleinert,[7] Smith,[8] Barrow,[9] Graminski,[10] Byrne and Weiner,[11] Kantrowitz,[12] Venter,[13] Cardwell,[14] and Gray.[15] Much of this work was directed toward color reversion.

The permanence of paper can be studied from the standpoint of (1) composition, (2) environment, and (3) significance of test data with respect to changes that occur during aging. These three approaches are interdependent.

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Under composition one might list:

a) aldehyde
b) ketone
c) carboxyl
d) salt of carboxyl
e) hemicelluloses
f) lignin
g) fibre, fibre length and degree of polymerization
h) crystallinity, or order
i) acid incorporated during manufacture
j) other additives.

Under environment one might list:

a) oxygen and ozone
b) moisture
c) smog and other impurities in the atmosphere
d) light
e) heat.

Reactions that might occur during the natural aging of paper include:

a) hydrolysis
b) oxidation
c) crosslinking
d) changes in order, or crystallinity, due to changes in moisture content
e) photolysis
f) photosensitization
g) photo-oxidation

Thermal decomposition must also be considered during accelerated aging, but it probably does not occur during natural aging unless the storage temperature is excessively high.

This report reviews the structure and basic reactions of cellulose in relation to the aging of paper and the effects these reactions might have on the measurable properties of paper. Also included is a discussion of some special reactions that normally occur due to environmental conditions, but are greatly influenced by composition of the paper.

2. Potential Chemical and Physical Changes in Cellulose and Paper

2.1 *Overview*

Hundreds of articles have been written describing reactions of cellulose dispersed in aqueous solutions of various reagents. The actual reactions that occur during the aging of paper have received little attention in the literature. This is no surprise, for "solid state" reactions of this type are not easy to follow. The *effects* of these reactions are evident from changes in physical and chemical tests, but these tests seldom describe *what* happens. Functional group analysis (aldehyde, carboxyl, ketone) is elusive, and Browning and Wink[4] found little change in functional group content during aging. However, the metal on the carboxyls greatly influences the course of decomposition during differential thermal analysis.[16]

Moisture relationships in the degradation of cellulose have not been properly identified. Supposedly, at low moisture contents, water exists on cellulose as a monomolecular layer.[17] The differential heat of swelling (ΔH) and the free energy changes (ΔF) vary greatly with moisture content and with temperature. The relative humidity necessary to maintain a given moisture content increases somewhat with temperature. At constant relative humidity, the absolute vapor pressure of water increases dramatically with increase in temperature. This, in turn, decreases the partial pressure of oxygen. At accelerated aging temperatures, near 90°C, the rate of exchange of moisture with cellulose in equilibrium with a given vapor pressure of water would be orders of magnitude higher than at room temperature. Whether this higher rate of exchange of moisture and the differences in ΔH and ΔF would simply speed up reactions that occur at room temperature or cause other reactions to occur, is a matter for speculation.

Hydrolysis, oxidation, crosslinking, and changes in lateral order, or crystallinity, are possible reactions during the natural aging of paper. In addition, thermal decomposition must be considered during accelerated aging. The basic reactions that can occur during natural aging are fairly limited, but the conditions that make these reactions possible and their effects on paper properties are more extensive.

Degradition reactions may occur in the fibre and in the bonding areas between the fibres. As some physical tests are affected by changes in bonding (e.g. crosslinking as measured by wet strength) more than by changes in the fibre (depolymerization and its effect on tensile strength) or vice versa, this must be taken into consideration in the evaluation of data. Hydrolysis, oxidation, and crosslinking would occur in both the fibre and in the fibre bonding areas. In order to separate the effects of crosslinking in the fibre and in the bonding areas, it would be an interesting experiment to achieve crosslinking in fibres and then make paper from them. As there would be little crosslinking in the bonding area, one could separate the effects of crosslinking in the fibre and in the bonded area.

The effect of additives introduced during the papermaking process may have a profound effect on the behavior of paper during aging. For example, an additive may perform well as a bonding agent but degrade with time. Some wet strength resins are in this category. Another additive might perform well as a bonding agent, and be more stable than the cellulose.

2.2 *Hydrolysis*

The acetal linkages in cellulose are fairly stable in neutral and alkaline media, but are easily hydrolyzed in acid (rate increasing with hydrogen ion activity),[18] (pp. 991–1006). Although the homogeneous (cellulose in solution) hydrolysis of cellulose is a random process,[19] (p. 122), heterogeneous (cellulose fibre dispersed in acid) hydrolysis is more complex. The bonds are not equally accessible in the crystalline and less well ordered areas. Peeling reactions occur in hot alkali,[20] (p. 596).

The hemicelluloses are much more readily accessible and occur in the amorphous state in wood,[20] (p. 164), but may precipitate out in the crystalline state on cellulose fibres during lignin removal,[20] (pp. 510, 608). Model compounds related to the hemicelluloses are hydrolyzed at a much higher rate than cellulose,[20] (pp. 119; 21). As long as the hemicelluloses are in the amorphous state, their rates of hydrolysis will be much greater than that of cellulose. When crystallized onto cellulose, some hemicelluloses probably do not hydrolyze appreciably faster than cellulose,[20] (p. 510). As a large fraction of the bonding material in wood pulp papers may consist of hemicelluloses, their chemistry is germane to the stability of paper, especially with respect to the stability of interfibre bonding.

The hydrolysis of carbohydrate structures is enhanced by the presence of oxidized groups,[20] (pp. 123, 124). This probably explains the synergistic effect of oxygen and moisture in the degradation of cellulose[22] and cellulose acetate.[23]

The most significant work on the effect of chemical structure on hydrolysis that is germane to the aging of cellulose has been compiled by Sharples,[18] (pp. 993–996). Oxidation and cleavage at the No. 2 and No. 3 carbon atoms in the anhydroglucose ring (Fig. 1) leads to the formation of aldehydes and carboxyls. These structures cause an increase in the rate of hydrolysis, even when reduced to the dialcohol. Most dramatic is the discovery of evidence that an aldehyde group on the No. 6 carbon atom may increase the rate of acid hydrolysis as much as 70 times.[24] This effect can be eliminated by reduction of the aldehyde

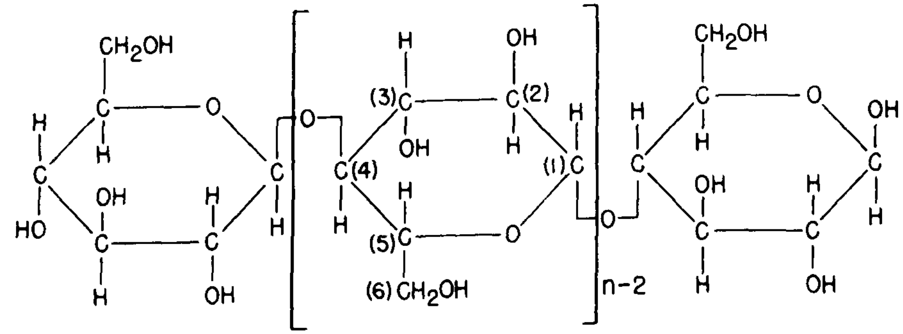

Fig. 1. Generally accepted formula of cellulose chain. Brackets enclose one molecule of anhydroglucose.

Figure 1. Formule générale de la chaîne de cellulose. La molécule de glucose en forme anhydride est représentée entre crochets.

Abbildung 1: Allgemein anerkannte Formel einer Zellulose-Kette. Die Klammern umschliessen ein Molekül Anhydroglukose.

back to hydroxyl with sodium borohydride. Wood cellulose is hydrolyzed at a higher rate than cotton cellulose, and it has been suggested that the reason for this is oxidation during pulping to give an aldehyde on the No. 6 carbon. When this is coupled with the higher rate of hydrolysis of the hemicelluloses, it is obvious that cotton fibre is likely to be more resistant to hydrolysis than wood pulp fibre.

It has been demonstrated that glycolic acid, a product of cellulose oxidation and hydrolysis, can react with glucose under certain conditions to give reversion products.[25] Thus, the aging of paper may involve a multitude of reactions between decomposition products and between decomposition products and cellulose. Rapson has shown that color reversion is caused by degradation products of oxidized cellulose.[26]

2.3 *Oxidation*

Little definitive work has been done on oxidation of carbohydrate structures during the aging of paper. Using the generally accepted formula for cellulose in Fig. 1, one can review the possibilities[19] (pp. 140–183).

1) The primary alcohol group on No. 6 carbon can be oxidized to aldehyde or carboxyl.

2) The secondary alcohol groups on carbons in the Nos. 2 and 3 position can be oxidized to ketone, either separately or simultaneously.

3) These same groups can be oxidized to aldehyde with cleavage of the ring, and then to carboxyl.

4) Although not an oxidative reaction, the sensitivity of the 2,3 dialdehyde to alkali is worth noting. The aldehyde in the No. 3 position is two carbon atoms removed from the ring oxygen. This is an example of the general case where alkaline cleavage can occur if an ether linkage is separated by two carbon atoms from an electronegative group, i.e. aldehyde. A similar instability would occur with an aldehyde group in the No. 6 position, or a keto group in the No. 2 or No. 3 position. Further oxidation of the 2,3 aldehydes to carboxyls stabilizes the structure.

The above oxidation reactions normally take place with cellulose dispersed in an aqueous solution of oxidant. Oxidation reactions that occur during the natural aging of paper would be expected to proceed with oxygen or ozone as oxidant. A subtle example of oxidation that is devastating to paper (but does not directly involve paper in the oxidation process) is the oxidation, catalyzed by manganese and iron impurities in the paper,[27] of sorbed sulfur dioxide to sulfur trioxide.

Kleinert[28] has shown that peroxide formation occurs during the accelerated aging of wood pulps at just under 100°C. Aging at high humidity produced much more peroxide than aging at low humidity. Strangely enough, aging at high humidity in nitrogen produced more peroxide than aging in air. Although much of the peroxide could be removed by washing with water, most remained with the pulp. While it is possible to follow aging by peroxide formation, peroxide also is destroyed during the process.[29] Kleinert[29] also showed that peroxide formation was several times greater in the fines than in the longer fibres in the pulp, and that peroxide was formed during air drying of pulp at 35°C.

Peroxide as an intermediate in the aging of paper should receive more attention, for cellulose basically is an ether. Ethers undergo oxidative degradation through peroxide formation,[30] (p. 77). The transition metals, including iron which occurs as a common impurity in cellulose, catalyze the decomposition of hydroperoxides,[30] (p. 42) and could be a factor in the degradation of paper.

The above oxidation reactions of cellulose also occur in the hemicelluloses. Some monomer units that occur in the hemicelluloses are shown in Fig. 2, and it is obvious that the units are very similar to anhydroglucose, the monomer unit of cellulose. The hemicelluloses normally are more accessible than cellulose and the building units may react much more rapidly with some reagents,[20] (pp. 119; 31). Therefore, this fraction of wood pulp paper should be more important to oxidative stability than the cellulosic fraction, especially as it is responsible for much of the interfibre bonding.

The fines probably represent the most vulnerable fraction of paper with respect to degradation. This is indicated by the much greater generation of

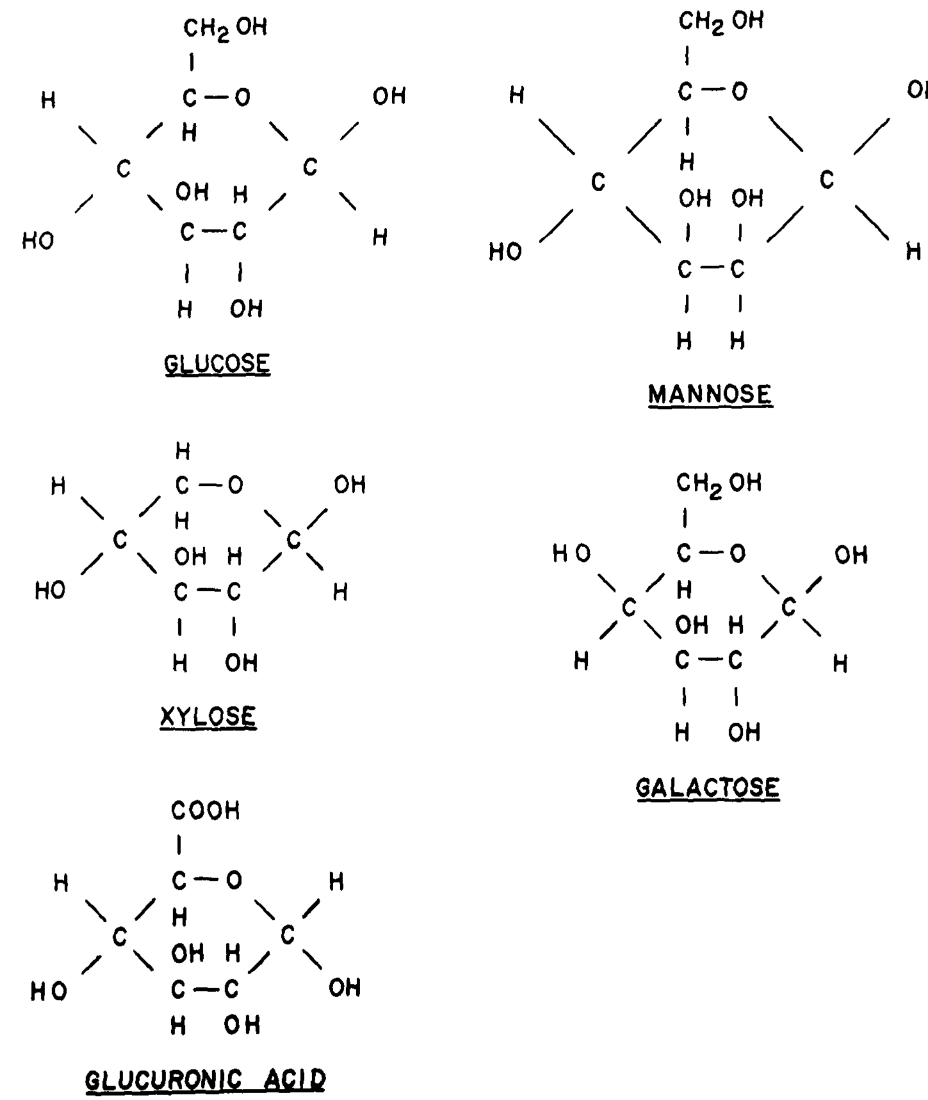

Fig. 2. Some monomer units of the hemicelluloses. *Polymers of mannose occur principally in softwoods and polymers* of xylose principally occur in hardwoods. Galactose is a minor constituent. Gluronic acid is an oxidation product of glucose and is a site for crosslinking (see text).
Figure 2. Quelques unités monomères des hémicelluloses. Les polymères du mannose existent principalement dans *les bois tendres*, tandis que les polymères du xylose sont trouvés principalement dans les bois durs. Le galactose est un constituant secondaire. L'acide gluconique est un produit d'oxydation du glucose et représente un point de réticulation (voir texte:.
Abbildung 2: Einige Monomereinheiten *von Hemizellulosen.* Polymere von Mannose treten prinzipiell *in weichen Hölzern* auf und polymere von Xylose treten prinzipiell in harten Hölzern auf. Galactose ist ein kleinerer Bestandteil. Glucuronsäure ist ein Oxidationsprodukt von Glukose und ein Ort für Netzverbindung (siehe Text).

peroxide in fines, as mentioned above. Fibre fraction studies show no real differences in chemical composition among the various fractions of chemical pulps except for the fines,[32] (p. 642). The fines in a bleached sulfite pulp contained most of the ash and hemicellulosic material, which was reflected in greater alkali solubility, higher copper number, and lower viscosity.

2.4 *Crosslinking*

Although crosslinking of cellulose has been known for years, it has been recognized only recently as a reaction that occurs during the aging of paper.[10]

Crosslinking in paper occurs at elevated temperature and is a consequence of conditions that could be described as accelerated aging, both in moist and in dry gases.[33,34,35] Back[33] has postulated that wet strength can develop as a result of a reaction between an aldehyde group on one chain with a hydroxyl group on a neighboring chain to form a hemiacetal. Presumably, a ketone on carbons 2 or 3 could form a hemiketal. Unless steric considerations prevent it, an aldehyde or ketone could form an acetal or ketal by reacting with adjacent hydroxyls with the elimination of water.

Back[33] has mentioned the possibility of formation of ether linkages between hydroxyls of adjacent chains by elimination of water. This certainly is a possibility, for this reaction takes place in an acidic solution of alcohol at around 110–130°C.[36] At higher temperatures an alkene is formed.

Ruffini[34] has presented evidence showing that crosslinking occurs by the formation of an ester linkage between carboxyl in one chain and a hydroxyl in a neighboring chain. He postulates that uronic acid groups in the hemicellulose fraction and, in unbleached sulfite pulps, sulfonic acid groups in the lignin, are responsible for the high strength level of paper made from certain pulps. The sheets Ruffini made from the experimental pulps were dried for three minutes at 130°C. As it should be possible for esters to be formed at this temperature, it would be interesting to prepare sheets by air drying without heat to determine the effect of the drying process on ester formation.

Regardless of the mechanism, wet strength development is catalyzed by aluminium sulfate, zinc chloride, ferric chloride, acids, and cupric nitrate.[33,35] Bach[33] has reported that the generation of wet strength is catalyzed by low pH and by metal ions with a high redox potential. He also found that salts that produce wet strength at a high rate also cause a rapid decrease in wet strength. This is especially true of those salts that release acids at elevated temperatures.

Improved bonding of cellulose fibres occurs after exposure to oxygen and ozone in a corona discharge. The bonding is further improved by soaking in 0.1

M sodium hydroxide after exposure to the corona discharge. These effects have been attributed to surface oxidation of the cellulose.[37]

2.5 *Changes in Lateral Order*

Changes in lateral order of cellulose in paper would be expected to affect most physical properties of paper. The discussion here will be confined to change in order that may occur in the bonding areas of paper. Recrystallization has been reported to occur during heterogeneous hydrolysis,[18] (pp. 996; 38). It has been reported that partially decrystallized cellulose recovered most of its crystallinity when exposed to moist air.[39] Extensive changes in physical properties of paper over a period of 36 years, apparently without changes in fibre strength,[40] are difficult to explain without assuming some change in the order of the system. Cellulose fibres change dimensions with changes in moisture content, and this is reflected in hygroscopic dimensional instability in paper. When pulp is dried and rewetted, the physical properties (wetting, strength, moisture regain) are never quite the same,[18](pp. 724;41). The properties of paper made from "broke", the waste paper from the paper machine, are significantly different from those of the paper from which it was made.[42] Luner[5] found that cycling of temperature and, therefore, relative humidity and moisture content, had an effect on physical properties of paper during accelerated aging.

From the above, it appears that, if conditions are favorable, crystallinity in the fibre may increase in water suspension or in a moist atmosphere. At the same time, the "order" that exists in the bonding regions of paper may decrease with time. This could seriously affect some physical properties without damaging the fibre. A possible explanation for this is that crystallization occurs with the exclusion of water, but requires the presence of water for the necessary mobility, whereas fibre to fibre bonding occurs through water bridges. With cycling of relative humidity, these water bridges probably can relax with time and affect the properties of paper that depend most on interfibre bonding. If some agent, such as rosin size, is present to enhance these bridges, they are less likely to relax with time. Chemical degradation with time in a sizing-bonded paper would affect those properties dependent on fibre intergrity.

It has been reported[43] that dialdehyde cellulose (carbons 2 and 3) and monocarboxyl cellulose (carbon 6) exhibit higher moisture regains than the unoxidized control. On the other hand, the moisture regain of dialcohol cellulose (reduced dialdehyde cellulose) was less than the unoxidized control. The heat of interaction of the samples with water showed the same trend. However, the levels of oxidation necessary to achieve these changes in moisture regain and heat of wetting were far higher than those which occur in the aging of paper. Therefore, oxidation is not likely to affect "order" or moisture regain in the bonding areas of paper as a primary effect.

The effects of destruction of bonding depend, in part, on the fibre length. In a long-fibred paper, fold, for example, might be affected hardly at all; but in a short-fibred paper, fold would be drastically reduced.

2.6 *Thermal Decomposition*

A property that often is overlooked in the *accelerated* aging of paper is the purely thermal instability of cellulosic and noncellulosic carbohydrate structures. This thermal instability should be more pronounced with increasing amounts of oxidized cellulose and with increasing amounts of hemicelluloses. Thermal decomposition at various temperatures has been discussed by Schwenker,[44] who showed that thermal degradation occurs even below 100°C.

3. Probable Effects of Chemical and Physical Changes on Measurable Properties of Paper

3.1 *Overview*

The changes that might be expected to occur during the accelerated aging of paper are given in Table 1 along with anticipated effects on various laboratory tests. Many of the reactions must occur concurrently or consecutively. Some may be isolated by excluding oxygen *or* moisture (or oxygen *and* moisture) from the aging atmosphere. This also may confuse the situation by preventing synergistic reactions from occurring.

The effects of various changes are listed as primary or secondary. A decrease in degree of polymerization (DP) is a primary effect of hydrolysis. Decrease in wet strength probably would be a secondary effect resulting from a general weakening of the structure.

3.2 *Hydrolysis*

During accelerated aging, hydrolysis could be expected to affect test properties as indicated in Table 1.

a) Degree of polymerization would be reduced by random attack in accessible areas.

b) Organic acids could be generated from carbohydrate structures, and protonic acid from aluminium complexes (if present).

Table 1. Reactions, or changes, that might occur during natural and accelerated aging of paper, and their expected effects on various tests.
Table 1. Réactions ou changements pouvant intervenir durant le vieillissment naturel et accéléré du papier. Effets attendus sur divers tests.
Tabelle 1: Reaktionen oder Veränderungen, die bei der natürlichen und beschleunigten Alterung von Papier auftreten können, und ihre voraussichtlichen Wirkungen auf verschiedene tests.

	Reaction or Change; P = Primary, S = Secondary									
Test	Hydrolysis		Oxidation		Crosslinking		Bonding "Order"[1] decrease		Thermal[2] Decomposition	
	P	S	P	S	P	S	P	S	P	S
DP[3]	↓		↓	↓	↑		--		↓	
Acid, H^+		↑	↑		--		--		↑	
Carboxyl		↑	↑			↓	--			
Aldehyde	↑		↑↓			↓	--		↑	
Ketone	--		↑			↓	--		↑	
Peroxide	--		↑		--		--		↓	
Moisture regain	--		↑↓		↓		↑			--
Alkali solubility	↑		↑		↓		--		↑	
Fold	↓		↓		↓			↓	↓	
Tear	↓		↓		↓			↑	↓	
Burst	↓		↓		↓		↓		↓	
Tensile	↓		↓		--			↓	↓	
Elongation	↓		↓		↓		↓		↓	
Modulus	↓		↓		↑		↓		↓	
TEA[4]	↓		↓		↓		↓		↓	
Zero span	↓		↓			↓	--		↓	
Wet tensile		↓		↑	↑		--			--
Blue reflectance		↓	↓	↓	--		--		↓	

1. Includes degradation of bonds formed by sizing agents.
2. Probably occurs only during accelerated aging.
3. Degree of polymerization.
4. Tensile energy absorption.

c) Aldehyde content would be increased, as one aldehyde group is formed with each hydrolytic chain break.

d) Carboxyl, ketone, and peroxide should not be affected.

e) Moisture regain should be relatively unaffected by chain scission, as the latter occurs in the accessible areas and none of the material is lost. During aging in a moist atmosphere, however, crystallization might occur with a decrease in moisture regain. In heterogeneous hydrolysis in acid solution, where the hydrolyzed material becomes soluble and is lost, the remaining cellulose is highly crystalline and has a low moisture regain,[18] (p. 736).

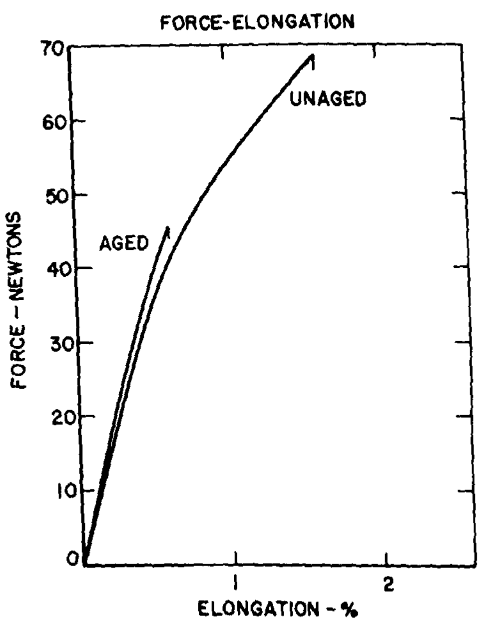

Fig. 3. Typical force-elongation curves for aged and unaged paper. Except for elongation, the two curves are not radically different.
Figure 3. Courbes tension-élongation de papiers soumis à un vieillissement ou sans vieillissement. A l'exception de l'élongation, les deux courbes ne diffèrent pas notablement.
Abbildung 3: Typische Kraft-Elongations-Kurven für gealtertes und nichtgealtertes Papier. Abgesehen von der Elongation sind die beiden Kurven nicht sehr unterschiedlich.

f) Alkali solubility should increase depending on the extent of hydrolysis. If hydrolysis is known to be the only reaction taking place, alkali solubility is an excellent diagnostic test.

g) Fold, tear, burst, tensile, elongation, and tensile energy absorption (TEA) would decrease. Modulus should decrease somewhat, but not extensively. Tensile, elongation, and TEA are increasingly sensitive, in that order, to a decrease in DP. This is illustrated in Fig. 3,[10] which shows typical load-elongation curves for an unaged specimen and an aged specimen of the same paper, whose retention of tensile strength, elongation, and tensile energy absorption are approximately 65 %, 35 %, and 25 %, respectively. In this particular sample, modulus has increased due to crosslinking.

h) Zero span would be decreased by fibre degradation, due to decrease in DP.

i) Wet strength would decrease as a secondary effect due to general weakening of the structure, or to hydrolysis of crosslinks as a primary effect.

j) Blue reflectance would not be expected to change if the cellulose is unaltered. However, this is never the case, and humic substances may be formed during hydrolysis[19], (p. 23). These may be dark in color and, therefore, would reduce the blue reflectance.

3.3 *Oxidation*

Oxidation of carbohydrate structures during aging of paper could be expected to affect test properties as indicated in Table 1.

a) A direct decrease in DP could be expected, partly as a result of increased sensitivity of oxidized structures to hydrolysis. Although viscosity measurements are a function of DP, viscosity solvents for cellulose usually are alkaline and are likely to cause chain scission,[19] (p. 147). An alternate approach is to nitrate the cellulose and dissolve in acetone for measurement of viscosity,[45] but this procedure has its own set of problems, especially with wood pulps.[46]

b) Carboxyl, aldehyde, ketone, and peroxide would be expected to increase, although aldehyde might also decrease, depending on the specific reaction. Low molecular weight oxidation products with an appreciable vapor pressure would be lost. Peroxides would be expected to form *and* decompose, so for a given set of experimental conditions, peroxide concentration should stabilize at a steady state value.

c) Moisture regain should decrease as a secondary effect due to crosslinking reactions,[18] (p. 857).

d) Alkali solubility should increase with oxidation and should be a sensitive test, but not a diagnostic one.

e) All of the physical properties, except wet strength, should decrease with oxidation, especially with the synergistic action of oxidation and hydrolysis.

f) Blue reflectance should decrease with oxidation. Saturated organic compounds (no double bonds) absorb in the ultraviolet, and the absorption moves up to the blue end of the visible spectrum only after the formation of a conjugated system of double bonds.[47] As it is not possible to form a conjugated system *between* anhydroglucose units in cellulose, because of the presence of an oxygen bridge, a conjugated system can exist only on carbons 1, 2, and 3 in the anhydroglucose ring, and on 1 only when it is terminal. Therefore, absorption in the visible due to oxidation of cellulose and hemicellulose is likely to occur only in the blue. Oxidation of hemicellulose in wood pulp is far more probable than oxidation of cellulose.

3.4 *Crosslinking*

Crosslinking could be expected to affect the tests listed in Table 1 as follows:

a) Some crosslinking should increase the molecular mass, and eventually crosslinking may render the material insoluble.[48] This may or may not show up in a viscosity determination, as some viscosity solvents may destroy the crosslinks.

b) Carboxyl[34] could be consumed in ester formation, and aldehyde and ketone[33] could be consumed in acetal and ketal formation, respectively.

c) Moisture regain should be decreased by crosslinking,[18] (p. 857). The structure would become more rigid and less accessible to moisture.

d) Alkali solubility should decrease unless the crosslinks are decomposed in alkali.[48]

e) Fold, tear, and burst deteriorate with crosslinking.[49] Changes in tensile strength will depend on the extent of crosslinking. Elongation decreases with crosslinking,[50] modulus increases,[10] and TEA should decrease as a function of decrease in elongation. Zero span should not be affected except as a secondary effect of fibre degradation if crosslinking occurs due to the presence of an acid catalyst.

f) Wet tensile increases significantly with crosslinking.[33]

g) Blue reflectance should not be affected.

3.5 *Changes in Bonding*

A discussion of decrease in order in the bonding area will be confined to (1) decrease in bonding due to decrease in "order" of the cellulose in the bonding area (conjecture at the moment), and (2) degradation of bonds formed by sizing agents. Concepts of the nature of fibre bonding and of sheet formation are changing rapidly but a good introduction to the subject is given by Casey.[32] Graminski[51] has shown that the film-like material created by the "fines" in paper affects properties, especially durability, in a way not previously anticipated. Apparently, failure occurs first in the "fines" area and not in the fibre to fibre bonding.

The bonding in paper depends on a host of variables such as type of fibre, extent of beating, wet pressing, sizing agents, carboxyl groups, zeta potential, and many others. McKee[42] has shown that repulping degrades those properties that are a direct function of fibre strength and fibre bonding, but those properties such as tearing strength, that are inversely related to bond strength, increase with the number of repulpings. This is not the same situation as degradation of bonding in a sheet of paper, but it may indicate that tearing strength would increase, or decrease more slowly, if degradation of bonding were the dominant reaction during aging.

As so little is known about selective degradation reactions in the bonding area of paper, the indications in Table 1 are conjecture only. Bonding is discussed because degradation of bonding and its effect on the properties of aged paper have been largely overlooked.

3.6 *Thermal Decomposition*

As a result of thermal decomposition, one would expect DP, all physical properties, and blue reflectance to decrease. Carboxylic acid content probably would decrease due to decarboxylation.

4. Some Special Situations

4.1 *Overview*

The above discussion is basic to an understanding of the natural aging of paper and the effects of aging on paper properties. Several specific situations related to the aging of pulp and paper deserve special attention, such as catalytic action of metals, generation of acid from unsuspected sources, and the potential of air pollutants for causing damage to paper. Although these examples of degradation are generated mostly by environmental factors, papers that are damaged most extensively have the seeds of their own destruction built into them.

4.2 *Metals as Catalysts*

Although the deleterious effect of sulfur dioxide on paper has been long recognized,[52] Langwell apparently was the first to show that the oxidation of sulfur dioxide was catalyzed by metallic impurities such as manganese and iron in paper, to sulfur trioxide.[27] Hudson and Milner[53] were able to detect the pickup of sulfur dioxide within two hours using radioactive sulfur as a tracer. Hudson,[54] Smith,[55] and Scribner[56] have shown that books stored in libraries in urban areas are more acid than books stored in rural areas. Pickup of sulfur is especially noticeable at the edges of pages in books, and Langwell[27] showed that the sulfate content was higher at the edges. This was noted earlier by Jarrell.[57]

The effect of certain metals that promote crosslinking already has been mentioned.

Several investigators[58, 59, 60] have shown that metals act as catalysts in brightness reversion.

4.3 *Effect of Chlorinated Extractives*

Bergman et al[61] have shown that removal of extractives can reduce color reversion. It also has been shown that chlorinated lignin[62] and chlorinated extractives[63] cause serious brightness reversion during accelerated aging. Chlorinated

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extractives release hydrochloric acid at comparatively low temperatures and cause brightness reversion of pulp during storage.

4.4 *Migration of Impurities*

Barrow[64] has reported on the migration of various impurities in paper. He showed that acid could migrate from one sheet to another and appreciably decrease the folding endurance. Examples of migration of impurities from sheets containing groundwood to fully bleached papers are quite common. It is not known whether the migration of colored impurities affects permanence.

4.5 *Air Pollutants*

The effect of air pollutants on the stability of paper has received little attention in the laboratory, with the exception of sulfur dioxide. The problem could be more serious than is suspected, for urban atmospheres contain several compounds that could be injurious to paper.[65] The possibility that certain metals may catalyze reactions of air pollutants with paper, or that some functional groups may cause paper to be more susceptible, cannot be overlooked. For various large cities in the U.S.A. mean values for 1964 for various gaseous pollutants in parts per million are as follows:[66]

	Range of Means	Maximum
Carbon monoxide	5 –12	60
Hydrocarbons	2 – 3	20
Sulfur dioxide	0.01– 0.18	1.62
Nitric oxide	0.03– 0.09	1.35
Nitrogen dioxide	0.03– 0.06	0.79
Total oxidants	0.02– 0.03	0.85

Aldehydes may run as high as 1.87, with a normal range of 0.5–0.60. Ozone may run as high as 0.90 with a normal range of 0.05–0.65.

Nitrogen dioxide has been found to degrade cotton, partially acetylated cotton,[67] and cellulose acetate film.[23] From these examples, it is obvious that air pollutants other than sulfur dioxide can give trouble.

5. Results of Some Recent Studies on Accelerated Aging of Paper

Venter[13] conducted an extensive investigation of the aging of paper. Some of his conclusions are as follows:

1) Alkali solubility is a very useful test, for changes in alkali solubility may show up, due to formation of alkali-sensitive linkages, before changes in physical properties.

2) Degradation reactions that occur during the aging of paper are random and are not "peeling" or "unzipping."

3) Chain length distribution provides very useful information, but the test is most time-consuming.

4) Sharp changes in slopes of plots of degradation rates against temperature occur at about 70°C with tear, fold, and alkali solubility.

5) Copper number (and therefore, reducing power) increases with time of aging.

6) The presence of rosin does not cause paper to be less stable during aging when change in alkali solubility is used as a criterion.

Cardwell[14] studied several variables associated with the aging of handsheets and commercial papers, and some of his conclusions are as follows:

1) If a crosslinking reaction occurs during the aging of paper, paper with a high bonding volume should develop crosslinks more rapidly during aging. (This probably is the reason that papers made from highly beaten stock are considered to be less stable than papers made from mildly beaten stock.)

2) ". . . more information is needed on the chemical and physical reactions contributing to loss in paper permanence over a temperature range before the Arrhenius relationship can be used with confidence to predict paper permanence."

3) An increase in interfibre bonding – presumably crosslinking – occurs during aging. (Cardwell suggests that water bridges may be replacd by direct hydrogen bonding between cellulose chains. It is more likely that disappearance of water bridges would "relax" bonding, so crosslinks would be formed by some other mechanism.)

4) The three tests for best predicting the stability of paper are tensile energy absorption, tensile breaking length, and force to give 300 folds. (On the basis of changes that occur in the force-elongation curve during aging, the sensitivity and usefulness of tensile breaking length might be questioned.)

5) Cycling of temperature and relative humidity increased the rate of degradation over that which occurred under constant conditions of temperature and relative humidity.

Neither Browning and Wink[4] nor Venter[13] found an increase in carboxyl content during accelerated aging. As any increase in carboxyl probably would be small, and as oxidized structures may become alkali-sensitive or soluble due to chain scission, the analytical tools presently available are not likely to be capable of measuring, or detecting, *changes* in carboxyl due to natural or accelerated aging.

Several investigators[4,13,23,15,68] have used Arrhenius plots as a tool in the evaluation of accelerated aging data. This approach has merit only if properly used within the limitations of (1) knowledge of the reactions involved and (2) mathematical treatment of data.[69,70,71] A far more useful approach should be to probe the reactions that occur during natural aging and devise accelerated aging conditions that cause these same reactions to occur.

6. Recommendations

1) The following tests should be useful in determining *what* happens during the aging of paper:

a) Zero-span tensile (fibre strength)
b) Wet tensile (crosslinking)
c) pH (generation of acid)
d) Alkali solubility (some chain scission and alkali sensitivity)
e) Functional group content (oxidation)
f) Molecular chain length distribution (chain scission and randomness of chain scission)
g) Peroxide formation (probably oxidation, but peroxides apparently can be formed in cellulose in the absence of air)
h) Oxygen sorption (oxidation)

2) The following tests should be usefull for *detecting* changes during the aging of paper, but are not particularly useful for identifying the nature of the change:

a) Folding endurance
b) Tearing strength
c) Elongation
d) Tensile energy absorption
e) Alkali solubility
f) Copper number
g) Viscosity

Alkali solubility appears under both (1) and (2). Without additional information, it belongs under (2); with information on functional group content, change in zero-span tensile, viscosity, and peroxide content, it can be evaluated properly and belongs under (1).

3) Other tests that may be somewhat less useful are:

a) Tensile strength
b) Burst

4) The following *general* conditions for accelerated aging should be evaluated:

a) Low temperature (50°–70°C)
b) Cycling of relative humidity, probably between 0 % and 70 % on hourly cycles.
c) Oxygen atmosphere

5) General guidelines for the composition of permanent record paper (not for specification purposes) are as follows:

a) Low functional group content (aldehyde, carboxyl, ketone)
b) Alkaline filler, or pH in the neutral range
c) Stable sizing material
d) Large percentage of long fibres (2–3 mm)
e) Low percentage of fines
f) No lignin
g) No aluminum salts during manufacture

6) Recommendations for future work

a) Examine papers that have been in storage for some time and attempt to identify the changes that have taken place during storage.
b) Devise one or more accelerated aging methods that cause these same changes to occur.

7. Abstracts and Summaries

Various reactions that cellulose can undergo are reviewed in relation to their bearing on the aging of paper. The principal reactions of cellulose are hydrolysis, oxidation, crosslinking, change in lateral order in the bonding area, and, during accelerated aging, thermal decomposition. The effects these various reactions might have on tests that are available for evaluating changes that occur during the aging of paper are reviewed. Some special examples of these reactions that occur during natural aging, because of special composition characteristics of the paper, are discussed. Suggestions are made concerning most sensitive tests for use in detecting changes in paper and tests, regardless of sensitivity, available for determining *what* happens during aging. Some general guidelines regarding specifications for permanent record papers are discussed.

1) The predominant chemical reactions in accelerated aging are hydrolysis, oxidation, and crosslinking. In some cases, especially waterleaf papers, a decrease in bonding order may be predominant.

2) Hydrolysis and oxidation are synergistic.

3) Hydrolysis in a heterogeneous system is especially enhanced by an aldehyde on the No. 6 carbon of anhydroglucose.

4) Hydrolysis is catalyzed by acid.

5) Aluminum catalyzes degradation.

6) Aluminum, other metals, and acids enhance and also destroy crosslinking.

7) Under proper experimental conditions, aldehydes and carboxyls enhance crosslinking.

8) Cycling of moisture content degrades physical properties of paper.

9) Some degradation reactions cause a decrease in moisture regain.

10) Moisture greatly enhances some types of degradation.

11) The "fines" in paper contribute significantly to the degradation of paper.

12) It is obvious from a review of the literature on accelerated aging of paper that:

a) Accelerated aging conditions that would satisfy all possibilities are impossible to define.
b) An accelerated aging test does not tell what a paper will be like after 25 or 50 years of storage. It only provides information concerning the ranking of different samples with respect to storage properties.
c) Some conclusions can be drawn concerning aging conditions.
d) Some conclusions can be drawn concerning useful tests for evaluation of aging.
e) Published data do not give a coherent picture of the aging of paper.
f) Most of the data are of limited utility because the samples were not adequately defined.
g) Arrhenius plots must be used with caution in the evaluation of stability.
h) The correlation of natural aging with accelerated aging is never likely to be perfect, or even high, as different natural aging conditions produce different results[55,72].
i) Extensive mathematical treatment of data, and predictions of stability based on these treatments, are not likely to be very fruitful.

Les divers tests et réactions de résistance de la cellulose au vieillissement sont passés en revue. Les réactions principales s'appliquant à la cellulose sont l'hydrolyse, l'oxydation, la réticulation, la modification de séquence latérale au niveau des liaisons et, durant les essais de vieillissement accéléré, la décomposition thermique. Les effets potentiels produits par ces diverses réactions lors des tests d'évaluation des changements intervenus durant le vieillissement du papier sont également passés en revue. Quelques exemples spéciaux de réactions intervenant durant le vieillissement naturel du papier en fonction des caractéristiques spéciales rattachées à la composition sont présentés. Diverses suggestions sont formulées concernant d'une part les tests à niveau de sensibilité élevée, utilisés pour la détection de changements dans le papier et d'autre part les tests disponibles – indépendamment de leur sensibilité – susceptibles d'expliquer les phénomènes intervenant lors du vieillissement. Quelques règles générales concernant les spécifications valables pour les papiers permanents d'enregistrement font l'objet d'une discussion.

1) Les réactions principales d'ordre chimique intervenant lors du vieillissement accéléré sont l'hydrolyse, l'oxydation et la réticulation. Dans quelques cas, spécialement avec les papiers sans apprêt une chute de séquence des liaisons peut représenter le facteur prédominant.

2) Existence d'une synergie entre l'hydrolyse et l'oxydation.

3) L'hydrolyse dans un système hétérogène est spécialement accrue par un aldéhyde sur l'atome de carbone No. 6 du glucose en forme anhydride.

4) L'hydrolyse est catalysée en milieu acide.

5) L'aluminium catalyse la dégradation.

6) L'aluminium, divers métaux et les acides produisent un accroissement et une rupture des liaisons de réticulation.

7) Dans des conditions expérimentales adéquates, les aldéhydes et les carboxyles accroissent la réticulation.

8) Des changements cycliques de teneur en humidité conduisent á une baisse des propriétés physiques du papier.

9) Certaines réactions de dégradation amènent une baisse du taux de réhumidification.

10) L'humidité accroît considérablement certains types de dégradations.

11) La présence de «fines» dans le papier contribue de façon évidente à la dégradation du papier.

12) Un passage en revue des données bibliographiques sur le vieillissement accéléré du papier conduit aux constatations suivantes:

a) Impossibilité de définir des conditions de vieillissement accéléré satisfaisant l'ensemble des situations.
b) Un essai de vieillissement accéléré ne peut révéler l'état éventuel du papier à l'issue d'une période d'entreposage de 25 à 50 ans. Il fournit seulement des informations concernant un classement relatif des différents échantillons vis-à-vis des propriétés d'entreposage.
c) Quelques conclusions peuvent être tirées au sujet des conditions de vieillissement.
d) Quelques conclusions peuvent être tirées concernant des tests utiles d'évaluation du vieillissement.
e) Les données publiées ne fournissent pas une vue d'ensemble cohérente du vieillissement du papier.
f) La majorité des données offre une utilité limitée du fait que les échantillons n'ont pas été définis de façon adéquate.
g) Les fonctions suivant la loi d'Arrhénius doivent être utilisées avec précaution lors de l'estimation de la stabilité.
h) Le degré de corrélation existant entre le vieillissement naturel et le vieillissement accéléré ne peut jamais être parfait ou même élevé, étant donné que diverses conditions de vieilissement naturel conduisent à des résultats différents (55, 72).
i) L'interprétation mathématique des données et les prédictions de stabilité basées sur le traitement de ces données n'offrent que des possibilités réduites relativement peu fructueuses.

Die verschiedenen Reaktionen, denen Zellulose ausgesetzt werden kann, werden in Bezug auf das Verhältnis zur Alterung von Papier untersucht. Die prinzipiellen Reaktionen von Zellulose sind: Hydrolyse, Oxidation, Vernetzung, Veränderung der seitlichen Reihenfolge in der Bindefläche und, bei der beschleunigten Alterung, thermische Zersetzung. Die Auswirkungen, die die verschiedenen Reaktionen auf die Tests haben können, die wir zur Einschätzung der Veränderungen haben, die bei der Alterung von Papier auftreten, werden beleuchtet. Einige spezielle Beispiele dieser Reaktionen, die sich bei der natürlichen Alterung auf Grund der besonderen Zusammensetzungseigenschaften zeigen, werden diskutiert. Es werden Vorschläge für sensitive Tests zur Ermittlung der Veränderungen in Papier unterbreitet, sowie Tests, die unabhängig von der Sensitivität, zur Bestimmung dessen zur Verfügung stehen, *was* während der Alterung geschieht. Es werden einige generelle Richtlinien zu den Spezifikationen von Karteikarten-Papier diskutiert.

1. Die vorwiegenden chemischen Reaktionen bei der beschleunigten Alterung sind Hydrolyse, Oxidation und Vernetzung. In einigen Fällen, besonders bei Wasserzeichen-Papier, kann eine Zersetzung der Verbindungsfolge überwiegend sein.
2. Hydrolyse und Oxidation sind synergistisch.
3. Die Hydrolyse in einem heterogenen System wird besonders durch ein Aldehyd von Karbon 6 der Anhydroglukose verstärkt.
4. Hydrolyse wird durch Säure katalysiert.
5. Aluminium katalysiert Qualitätsabbau.
6. Aluminium, andere Metalle und Säure erhöhen und zerstören die Netzverbindung.
7. Unter guten Versuchsbedingungen verstärken Aldehyde und Carboxyle die Netzverbindung.
8. Das Durchlaufen des Feuchtigkeitsgehaltes vermindert die physikalischen Eigenschaften von Papier.
9. Einige Qualitätsabbau-Reaktionen rufen eine Entfettung des Feuchtigkeitsgehaltes hervor.
10. Feuchtigkeit fördert einige Formen des Qualitätsabbaus.
11. Die "Verfeinerungen" im Papier tragen deutlich zum Qualitätsabbau von Papier bei.
12. Bei einer Durcharbeitung der Literatur über beschleunigte Alterung von Papier zeigt sich deutlich, dass:

a) Bedingungen für die beschleunigte Alterung, die alle Möglichkeiten umfassen, können nicht definiert werden.
b) Ein Test über beschleunigte Alterung sagt nicht darüber aus, wie das Papier nach einer Aufbewahrung von 25 oder 50 Jahren aussieht. Wir erfahren nur, welche verschiedenen Lagerungseigenschaften die einzelnen Muster im Verhältnis zueinander haben.
c) Über die Alterungsbedingungen können einige Schlussfolgerungen gezogen werden.
d) Es können einige Schlussfolgerungen über nützliche Tests zum Abschätzen der Alterung gezogen werden.
e) Die veröffentlichten Daten vermitteln kein umfassendes Bild über die Alterung von Papier.
f) Die meisten Daten sind nur begrenzt von Nutzen, weil die Muster nicht genügend definiert worden sind.
g) Arrhenius-Diagramme zur Einschätzung der Stabilität sind mit Vorsicht zu verwenden.
h) Die Wechselbeziehung zwischen natürlicher Alterung und beschleunigter Alterung kann niemals perfekt sein, da die verschiedenen natürlichen Alterungsbedingungen zu verschiedenen Ergebnissen führen (tt, 72).
i) Eine umfassende mathematische Datenbehandlung und Voraussagen über Stabilität auf dieser Grundlage sind *nicht* besonders wertvoll.

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Microbiodeterioration of Audiovisual Collections

Part 1. Protection of Audiovisual Records Against Destructive Microflora

by E. CZERWIŃSKA & R. KOWALIK

Damaging Factors

The permanence of audiovisual materials depends among other things upon their chemical composition and on protection from harmful fumes and gases and from dust. Motion picture films and magnetic tapes are deteriorated by such *atmospheric pollutants*, as sulphur and nitrogen dioxides, sulphur trioxide, hydrogen sulphide and ammonia.[3,12,16,23,29–31,33,47,49] According to Carroll and Calhoun,[4] nitrogen dioxide in reaction with water forms nitric and nitrous acids and these cause serious degradation of sound recording materials. In about 2 hours silver images of black-and-white and colour images on triacetate tape fade severely. Within two days emulsion becomes sticky and after two weeks triacetate tape softens and deforms under the influence of nitrogen dioxide and high moisture content.

Dust and grit and other solid or liquid particles suspended in the air act as catalysts in the degrading processes of black-and-white negatives, of colour transparencies, motion picture films and magnetic tapes. This is a well recognized problem.[2,3,5,7,10,14,15,18,21,22,27,28] As a result of damages caused by them the playback quality of magnetic tapes becomes worse. Dust particles deposit on the preserved audiovisual collections impairing their comprehension and pleasure to the ear and cause not only mechanical damage (emulsion scratching), but may become also indirect sources of chemical and biological degradation.[2,6,7,13,16,23,24,34,35–45,50–52] Dust covering on audiovisual tapes attracts moisture and this minimal amount of water, together with gaseous atmospheric pollutants such as nitrogen and sulphur dioxides, leads to compounds exceedingly dangerous to sound recording materials. Small amounts of water attracted to tapes by dust constituents are also sufficient to start the growth of fungi, because spores and mycelium fragments are already present on the surface of dust particles. Therefore occasionally even with air conditioning

Restaurator 3/1979: 63–80.
0034-5806/79/010063-18 $ 02.50/0 © 1979 Munksgaard. Copenhagen.

Table 1. The more important fungi- and bactericides proposed to cellulosic and collagenic materials.
Table 1. Liste des fongicides et des bactéricides le plus importants proposés pour la protection des matières cellulosiques et des collagènes.
Tabelle 1: Die am häufigsten auftretenden Pilze- und Bakterizide, die zum Schutz von Zellulose- und Kollagenmaterialien vorgeschlagen werden.

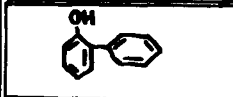
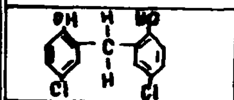
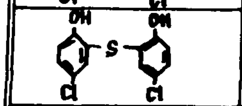
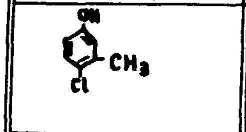
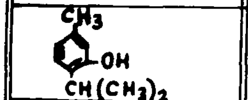
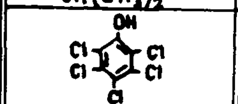
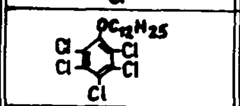
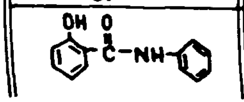
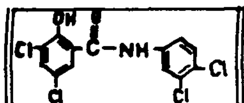
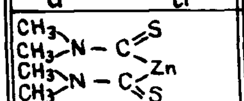
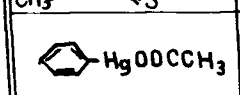
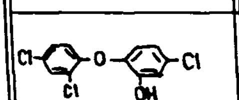
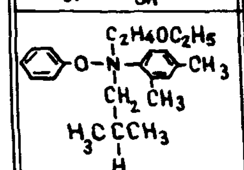
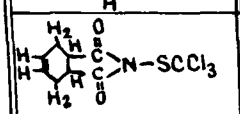
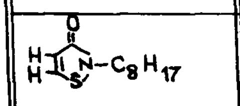
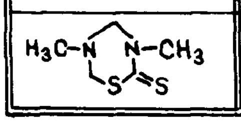
Structural formula	Chemical name	Trade name	Field of application	Melting point	Colour	Solubility	Toxicity	Remarks
	o-phenylphenol	Preventol O Dowicide A	cellulosics, wax, seals, inks	57°C	colourless	in most organic solvents	LD_{50} to rats 2,48 g/kg p.o.	sodium salt soluble in water, acetone, alcohol, insoluble in petrol oil
	2,2'-dihydroxy-5,5'-dichlorodi-phenylmethane	Dichlorophene Preventol GD, B4, DDM, DDDM	cellulosics, glues, paints, varnishes	177–178°C	pure compound colourless, commercial comp. tan coloured	slightly soluble in ethyl alcohol, acetone	LD_{50} to dogs 2g/kg p.o.	alcali salt soluble in water
	2,2'-dihydroxy-5,5'-dichlorodi-phenyl monosulfide	Fentichlor	collagenics		colourless	in water; 76% in ethanol	low toxicity	broad spectrum of activity in a great pH range
	4-chloro-3-cresol 6-chloro-3oxy-methylbenzene	Rashit Preventol CMK	cellulosics, glue, leather, paint, parchment, audio-visual materials, disinfection of storerooms	66°C	colourless	in most organic solvents	skin irritating	sodium salt soluble
	isopropylcresol	Thymol	cellulosics, (parchment)	49–51°C	colourless	ethyl alcohol, carbon sulphide, glacial acetic acid, ethyl ether, oils, slightly soluble in water, glicerol	probable LD to humans 50–500 mg/kg p.o. skin irritant in concentration higher than 2%	
	pentachlorophenol	PCP, penta	cellulosics	191°C	tan coloured	in most organic solvents	LD_{50} to rats 210 mg/kg p.o. skin irritant easily absorbed by skin from air, food, water	sodium salt water soluble; gives in the light a red product
	lauryl penta-chlorophenol	Mystox, LPL, LSL	cellulosics, plastics, paints		colourless	benzene, acetone, oil, waxes, plastifiers		
	n-phenyl sali-cylamide	Shirlan	cellulosics leather, paints	135°C	cream coloured	in most organic solvents	low toxicity LD_{50} to rats higher than 2.000 mg/kg p.o.	
	3,5,3',4'-tetrachlo-rosalicylamide	Irgasan BS-200	cellulosics, plastics	161–163°C	white	in most organic solvents	low toxicity	
	zinc dimethyldi-thiocarbamate	Ziram (common name)	cellulosics, plastics	240°C	white	soluble in carbon di-sulphide, dilute alcalies, strong ammonia solution	low toxicity LD_{50} to rats 1400–1500 mg/kg p.o. recognized cancerogen	
	phenylmercuric acetate	PMA, PMAC, PMAS	cellulosics, paints	149–153°C	colourless	ethyl alcohol, acetone, benzene	highly toxic	
$(C_4H_9)_3SnOSn(C_4H_9)_3$	bis(tri-n-butyl-tin) oxide	TBTO	cellulosics, paints	180°C	colourless	miscible with most organic solvents	LD_{50} to rats 148 mg/kg p.o. may be absorbed by skin	
	2,4,4'-trichloro-2'-hydroxydi-phenylether	Irgasan DP-300	cellulosics	54–57°C	colourless	in most organic solvents	LD_{50} to rats 2,8g/kg p.o.	fungi-and-bactericide
	diisobutyl phe-noxy-ethoxy-ethyl dimethyl benzyl ammo-nium chloride	Hyamine 1622	cellulosics with emulsion		colourless	in water	low toxicity	
	N-(trichlorome-thylthio)-4-cy-clohexene-1,2-dicarboxymide	Captan (common name)	plastics, paints	178°C	white	partly in acetone, xylene, chloroform, benzene, toluene	LD_{50} to rats 5.000 mg/kg p.o.; may cause skin irritation	
	octyl-4-izothia-zolo-3-one	Kathon LP	collagenics		colourless	in water	LD_{50} to rats 3160 mg/kg p.o.	against fungi and bacteria G+ and G−
	dimethyl-thio-notetrahydro-thiodiazin	Dazomet, DMF, Cosan S	collagenics			in water	low toxicity	broad spectrum from 20–2.000 ppm at the pH from 4.0–9.0

Table 1. The more important fungi- and bactericides proposed to cellulosic and collagenic materials.
Table 1. Liste des fongicides et des bactéricides le plus importants proposés pour la protection des matières cellulosiques et des collagènes.
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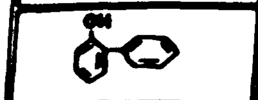
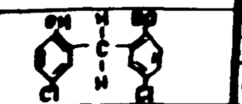
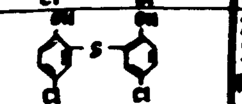
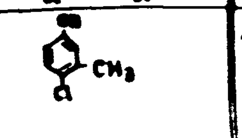
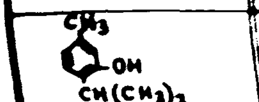
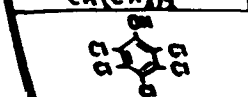
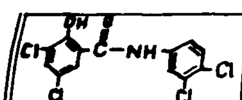
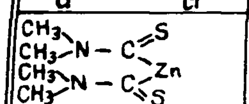
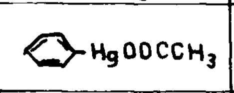
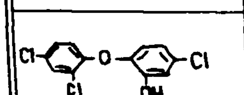
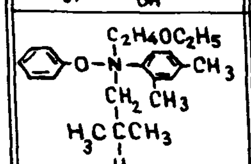
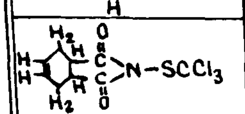
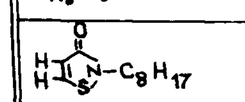
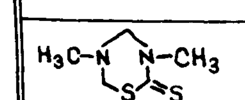
	o-phenylphenol	Preventol O Dowicide A	cellulosics, wax, seals, inks	57°C	colourless	in most organic solvents	LD_{50} to rats 2,48 g/kg p.o.	sodium salt soluble in water, acetone, alcohol, insoluble in petrol oil
	2,2'-dihydroxy-5,5'-dichlorodiphenylmethane	Dichlorophene Preventol GD, B4, 9004, 900M	cellulosics, glues, paints, varnishes	177–178°C	pure compound colourless, commercial comp. tan coloured	slightly soluble in ethyl alcohol, acetone	LD_{50} to dogs 2g/kg p.o.	alcali salt soluble in water
	2,2'-dihydroxy-5,5'-dichlorodiphenyl monosulfide	Fentichlor	collagenics		colourless	in water; 78% in ethanol	low toxicity	broad spectrum of activity in a great pH range
	4-chloro-3-cresol 6-chloro-3-oxy-methylbenzene	Raschit Preventol CMK	cellulosics, glue, leather, paint, parchment, audio-visual materials, disinfection of storerooms	66°C	colourless	in most organic solvents	skin irritating	sodium salt soluble
	isopropylcresol	Thymol	cellulosics, (parchment)	49–51°C	colourless	ethyl alcohol, carbon sulphide, glacial acetic acid, ethyl ether, oils, slightly soluble in water, glicerol	probable LD to humans 50-500 mg/kg p.o. skin irritant in concentration higher than 2%	
	pentachlorophenol	PCP, penta	cellulosics	191°C	tan coloured	in most organic solvents	LD_{50} to rats 210 mg/kg p.o. skin irritant easily absorbed by skin from air, food, water	sodium salt water soluble; gives in the light a red product
	lauryl pentachlorophenol	Mystox LPL, LSL	cellulosics, plastics, paints		colourless	benzene, acetone, oil, waxes, plastifiers		
	[illegible]	[illegible]	cellulosics	[illegible]°C	[illegible]	in most organic [illegible]	low toxicity LD_{50} to rats higher than [illegible] mg/kg p.o.	
	3,5,3',4'-tetrachlorosalicylamide	Irgasan BS-200	cellulosics, plastics	161–163°C	white	in most organic solvents	low toxicity	
	zinc dimethyldithiocarbamate	Ziram (common name)	cellulosics, plastics	240°C	white	soluble in carbon disulphide, dilute alcalies, strong ammonia solution	low toxicity LD_{50} to rats 1400-1500 mg/kg p.o. recognized cancerogen	
	phenylmercuric acetate	PMA, PMAC, PMAS	cellulosics, paints	149–153°C	colourless	ethyl alcohol, acetone, benzene	highly toxic	
$(C_4H_9)_3SnOSn(C_4H_9)_3$	bis(tri-n-butyl-tin) oxide	TBTO	cellulosics, paints	180°C	colourless	miscible with most organic solvents	LD_{50} to rats 148 mg/kg p.o. may be absorbed by skin	
	2,4,4'-trichloro-2'-hydroxydiphenylether	Irgasan DP-300	cellulosics	54–57°C	colourless	in most organic solvents	LD_{50} to rats 2,8g/kg p.o.	fungi-and-bactericide
	diisobutyl phenoxy-ethoxyethyl dimethyl benzyl ammonium chloride	Hyamine 1622	cellulosics with emulsion		colourless	in water	low toxicity	
	N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboxymide	Captan (common name)	plastics, paints	178°C	white	partly in acetone, xylene, chloroform, benzene, toluene	LD_{50} to rats 5.000 mg/kg p.o.; may cause skin irritation	
	octyl-4-izothiazolo-3-one	Kathon LP	collagenics		colourless	in water	LD_{50} to rats 3160 mg/kg p.o.	against fungi and bacteria G+ and G–
	dimethyl-thiotetrahydro-thiodiazin	Dazomet, DMF, Cosan S	collagenics			in water	low toxicity	broad spectrum from 20-2.000 ppm at the pH from 4.0 – 9.0

installations fungal problems of sound recording materials may be serious.[8,9,19,26,27,33]

Conditions of development of fungi depend on the relative humidity of the environment, on the moisture content of material, and also on the temperature, the acidity and the presence of nutrient sources. To initiate the growth of fungi, water sometimes in trace amounts is necessary. Although optimum temperature for fungal metabolism is in general between 24 and 26°C, and optimum for pH lies between 5.0–5.6, some species may vegetate in temperature as low as −7°C and up to +50°C, with pH ranging from 1.0 to 10.0 and relative humidity as low as 63 %.[1,12]

Fungi requirement as concerns nourishment are very different. Some species may develop on very minimal impurities or, after some period of time, even on hard degradable materials. The basic source of nutrient media for fungi and Actinomycetes vegetating on audiovisual tapes are impurities such as dust, fingerprints, etc., and also the main emulsion component which is gelatin. In certain cases additional carbon source for fungi may be waxes, used to improve steadiness of the projected image and to protect against friction and fingerprint traces.[17] Although the main synthetic resins with the exception of cellulose nitrate and cellulose acetate are fungi resistant,[20,32,33] fungi and Actinomycetes are still able to destroy the plastic in tapes.[3,7,16,23,25,26,33,38] In this case microorganisms utilize as nutrient source plasticizers, fillers, lubricants and extenders incorporated into magnetic tapes and motion picture films to obtain the necessary physico–chemical properties of these sound recorders.

Experimental Part

The damages caused by fungal activity, as observed in Polish sound recording archives on some motion picture films and magnetic tapes (Figs. 1, 2) clearly indicated the need for studies on the possibilities of protection of these records against microorganisms. Considering the character and susceptibility of emulsion upon various agents and the probability that the additives would interfere with photographic and sound properties of the emulsion, the killing of fungi, which develop on motion picture film and magnetic tapes was very compounded. It limits the possibility of the selection of biocide. We decided to not use, for the protection of motion picture films and magnetic tapes, the compounds, activity of which depends upon intermediate contact. Therefore utilization of fungicide effective in a vapour form only has been considered. Out of the chemical compounds of this type, 4-chloro-3-cresol seemed to us the most suitable (Table 1).

The program of the work in our laboratory was the following:

Isolation and identification of microorganisms occurring on sound recordings and in storage area.

Test of microbioresistance of bobbins (reels or spools) and sealing tapes.

Search for a method of protection of audiovisual recordings against microbial agents.

The isolation of fungi was carried out by three methods:

By direct streaking of fungi taken out from magnetic tapes or motion picture films on potato-dextrose agar medium/200 g of sliced potato + 1 liter of distilled water + 20 g of glucose and 17 g of agar-agar. pH was adjusted to 5.5.

By placing 2 cm long strips of films or tapes contaminated with fungi in Petri dishes, on potato-dextrose agar or on filter paper discs with the liquid culture medium of Greathouse, Klemme, Barker of pH = 5.5–5.6.[11]

By using the method of impressions. In this case sterilized filter paper discs were pressed against spots of microflora, growing on films or on magnetic tapes. These discs with fragments of mycelium or spores were transferred to Petri dishes, and 15 ml of the liquid medium of Greathouse, Klemme, Barker of pH = 5.5–5.6 was poured into every 100 mm Petri dish.

Microflora which exists in the air of particular air-conditioned and not conditioned storage area was isolated in the following way:

Sterilized Petri dishes with filter paper discs were placed at various parts of the storage area and left open for one hour. After that, 15 ml of Greathouse, Klemme, Barker liquid medium was poured into every 100 mm Petri dish.

All dishes with samples were incubated at a temperature of 24–26°C and 90 % of relative humidity during a period of three weeks. The developing colonies of fungi were transferred on potato-dextrose agar medium and after obtaining pure cultures the particular microorganisms were identified.

The microbioresistance of bobbins (spools or reels) and sealing tapes. These auxiliary materials also have been tested. Bobbins (spools or reels based on polyvinyl chloride) of different origin (Austrian, English, French, Polish, American) were placed in Petri dishes or desiccators in a humid atmosphere. One set of bobbins (reels or spools) was contaminated with a water suspension of 12 species of fungi spores isolated from motion picture films and magnetic tapes, and another identical set with a water suspension of spores of *Aspergillus niger*, *Penicillium funiculosum*, *Trichoderma viride* and *Chaetomium globosum*, as used to test the microbioresistance of synthetic materials, according to the International Standard Organisation method, ISO/DIS 846.[53] Also 50 mm long fragments of scotch or other sealing tapes were placed in Petri dishes on glass slides in a humid atmosphere and inoculated with fungi spores as previously. The determination of microbioresistance was made after 4 weeks of incubation at a temperature of 24–26°C and 90 % of relative humidity.

Methods of disinfection. Disinfection methods for audiovisual recordings have been tested in laboratory experiments and in store-room conditions. 4-Chloro-3 cresol at different concentrations has been chosen for the experiments.

In preliminary laboratory experiments the influence of vapour action of 4-chloro-3-cresol on fungi growing in Petri dishes on hardened potato-dextrose agar medium was investigated. The tests were also made on contaminated and non-contaminated strips of tapes, which were subjected in both cases to the vapour action of 4-chloro-3-cresol.

The tests were made in test tubes on sloped potato-dextrose agar medium or in Petri dishes on V shaped glass sticks. In the case of test tubes, loosely fitting cotton wool plugs were put inside the test tubes above hardened medium and on the surface of cotton wool plugs, filter paper discs soaked with 4-chloro-3-cresol were placed and the test tubes were tightly closed. In the case of Petri dish tests, sterilized distilled water-soaked filter paper was placed on the bottoms, and on the lids discs imbibed with fungicide were put in. The Petri dishes were sealed with tape. The evaluation of fungitoxic vapour action was made visually or under the microscope, after two weeks culture at a temperature of 24–26°C.

The tests carried out directly in the storage area included disinfection of contaminated motion picture films and magnetic tapes placed in sealed metal cans, having at the bottom or both at the bottom and at the lid filter paper discs soaked with ethanol solution of 4-chloro-3-cresol dissolved in 70 or 96 % ethanol. Bobbins (spools or reels) and cans were treated in the same way. Also experimental disinfection of air in the storage area was carried out by using in aerosol spray a 1 % or 2 % ethanol solution of 4-chloro-3-cresol at the amount of 1 g/m^3.

Results

It was found that the most often occurring fungi on motion picture films and magnetic tapes were the members of the genus *Aspergillus* (Fig. 3) and *Penicilium* (Fig. 4), besides that *Chaetomium* (Fig. 5), *Cladosporium* (Fig. 6), *Stemphylium* (Fig. 7), *Alternaria* (Fig. 8) and *Streptomyces*.

Out of the atmosphere of air conditioned store-rooms, as a rule, *Penicillium* and *Aspergillus* have been isolated.

Fig. 1. The colonies of fungi growing on magnetic tape.

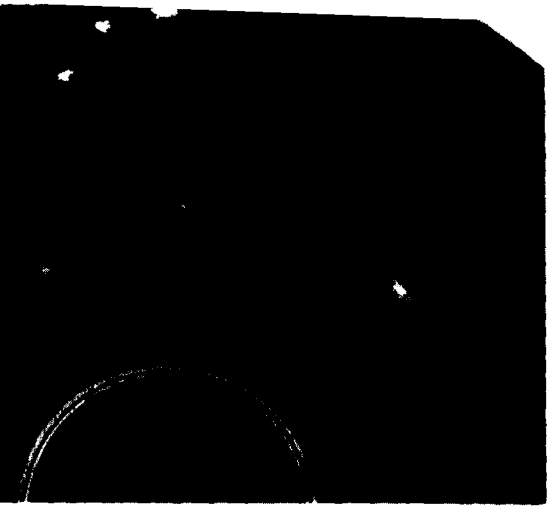


Fig. 2. The colonies of fungi growing on motion picture film.

Fig. 3. *Aspergillus sp.* (× 420).

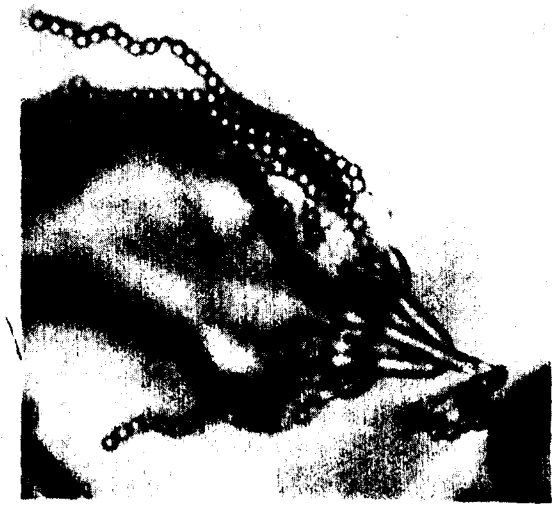


Fig. 4. *Penicillium sp.* (× 500).

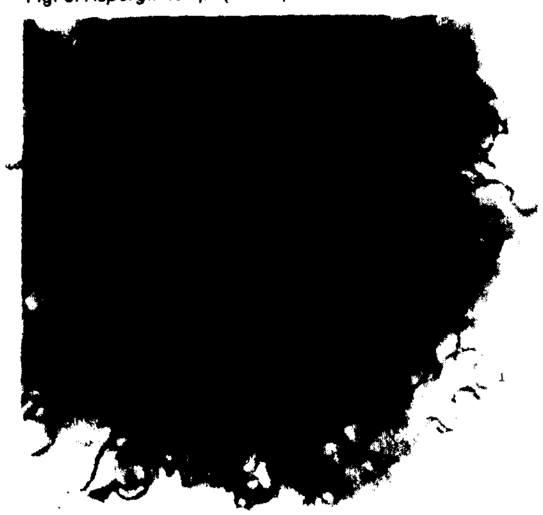


Fig. 5. *Chaetomium sp.* (× 120).

Fig. 6. *Cladosporium herbarum* (Persoon) Link (× 500).

Considering the results of our studies with different concentrations of 4-chloro-3-cresol in test tubes and Petri dishes upon fungi growing on agar media and on motion picture films and magnetic tapes contaminated with fungi, it was concluded that filter paper discs imbibed with 2.5 % solution of 4-chloro-3-cresol in 96 % ethanol inhibited completely the growth of fungi.

After 12 months of storing, no traces of fungal growth was observed on contaminated motion picture films and magnetic tapes, which were placed in the sealed metal cans, having at the bottom and at the lid filter paper discs soaked in 2.5 % ethanol solution of 4-chloro-3-cresol.

According to our experiments it is desirable, however, to clean the surface of heavily contaminated tapes or films before placing them in the cans. This treatment may be made with soft cloth or filter paper, which has been soaked in 2.5 % in 96 % ethanol solution of 4-chloro-3-cresol, and left until ethanol evaporates.

Not only fungi isolated from audiovisual materials and store-room atmosphere develop on the bobbins (spools or reels) but also the genuses utilized for the evaluation of microbioresistance of plastics. On the bobbins (spools or reels) of Polish, American (Kodak) and Austrian origin the most often occurring fungus was *Chaetomium globosum* Kunze. Therefore bobbins (spools or reels) should be disinfected too. Good results have been obtained by wiping contaminated bobbins (spools or reels) with well-squeezed soft cloth moistened with 2.5 % in 96 % ethanol solution of 4-chloro-3-cresol.

It was observed that disinfection of air-conditioned storage areas with aerosol of 1 % ethanol solution of 4-chloro-3-cresol at the amount of $1 g/m^3$ is sufficient, whereas in heavily dusted storage areas even a 2 % solution of 4-chloro-3-cresol was not sufficient. The most fungicide resistant were: *Aspergillus terreus* Link and sometimes *Chaetomium globosum* Kunze.

Part 2. Microbial Problems in Photographic Print Collections

Photographic prints are documents made on paper covered with a thin emulsion layer composed of gelatin and silver salts or other light sensitive chemical compounds.

Photographic print collections stored under conditions of relative humidity higher than 60 % and temperature of 24–26°C or higher are liable to damage by air-borne spores of fungi and Actinomycetes, which may utilize the gelatin in the emulsion layer as a carbon and nitrogen source. Silver salts and other compounds in the emulsion do not inhibit sufficiently the growth of microflora.

The growth of fungi and Actinomycetes occur on the print surface and cause

Fig. 7. *Stemphylium lanuginosum* Harz (× 100).

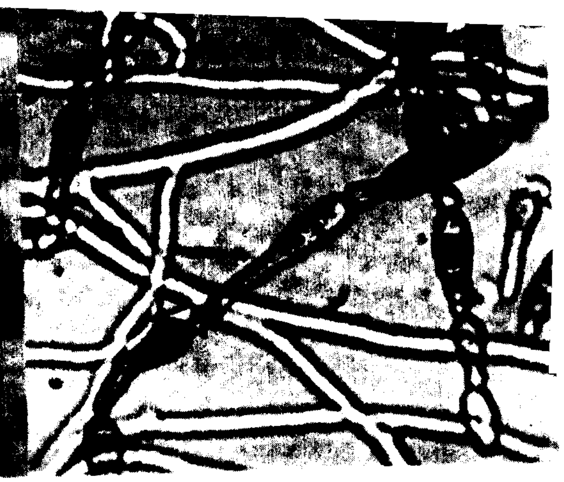


Fig. 8. *Alternaria sp.* (× 500).

Fig. 9. *Acrostalagmus cinnabarinus* Corda var. *nana* Oudemans (× 420).

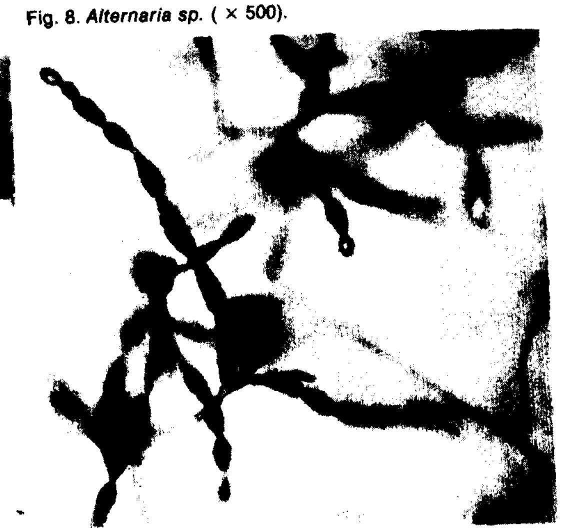


Fig. 10. *Alternaria tenuis* Nees (× 250).

Fig. 11. *Aspergillus amstelodami* Thom and Church (× 500).

Fig. 12. *Aspergillus candidus* Link (× 420).

coloured or dull spots.[46,47] As further consequence of the metabolism of microflora a complete destruction of the image and emulsion layer and a decomposition of the paper support may take place. Therefore it is necessary to protect photographic print documents against damages caused by microorganisms, by ensuring proper storage conditions, or by treatment with biocides. According to the propositions of Kodaks Customer Service Pamphlet AE-22[46] 1 % of Hyamine 1622 (diethyl-benzyl-tert-octylphenoxyethyl ammonium chloride) (Table 1) – protects black-and-white prints against harmful effects of fungi.

Experimental Part

The study of the problems of protection of photographic prints by utilizing biocides against microorganisms was started in our laboratory because climatic conditions in Poland and possible failures in air-conditioning installations may favour a prolific growth of microflora. At first the microorganisms that destroy black-and-white photographic prints were isolated and identified with the use of different cellulosic media.[1,19] The next stage of our work was to investigate preventive methods for the protection of photographic prints. Hyamine 1622 and the sodium salt of 4-chloro-3-cresol (Table 1) both in 1 % solutions in water were used.

The experiment was carried out in the following way: 50 × 50 mm squares of photographic prints were cut out with a sterile tool and placed in 100 mm Petri dishes on glass sticks:

1/3 of the number of prepared samples was sprayed with sterilized distilled water

1/3 of the number of samples was sprayed with Greathouse, Klemme, Barker medium[11] of the following composition:

K_2HPO_4	1.3940 g
$MgSO_4$	0.7395 g
NH_4NO_3	1.006 g
$CaCO_3$	0.005 g
NaCl	0.005 g
Fe, Zn and Mn as SO_4 salts	0.001 g
Distilled water	1000 ml

1/3 was sprayed with a suspension of spores of *Aspergillus niger, Aspergillus terreus* and *Penicillium brevi-compactum* in Greathouse, Klemme, Barker medium.

Fig. 13. *Aspergillus flavus* Link (× 500).

Fig. 14. *Aspergillus niger* van Tieghem (× 500).

Fig. 15. *Aspergillus terreus* Thom (× 250).

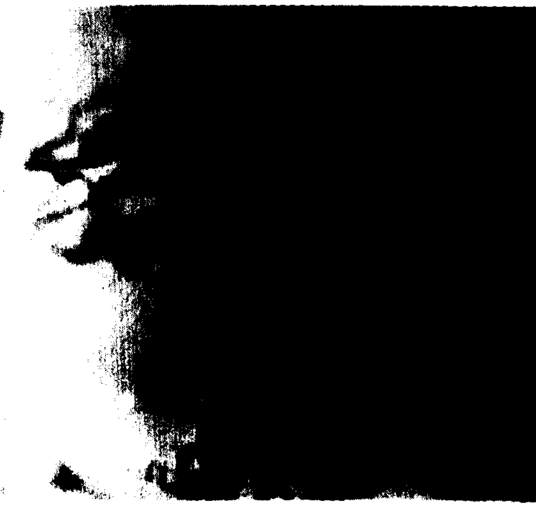


Fig. 16. *Chaetomium globosum* Kunze (× 250).

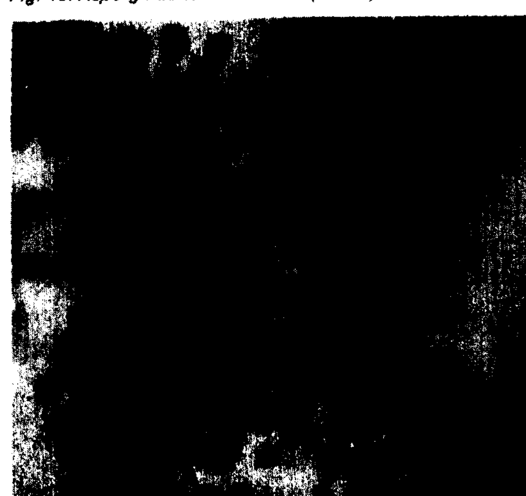


Fig. 17. *Fusarium* probably oxysporum Schlechtendahl (× 250).

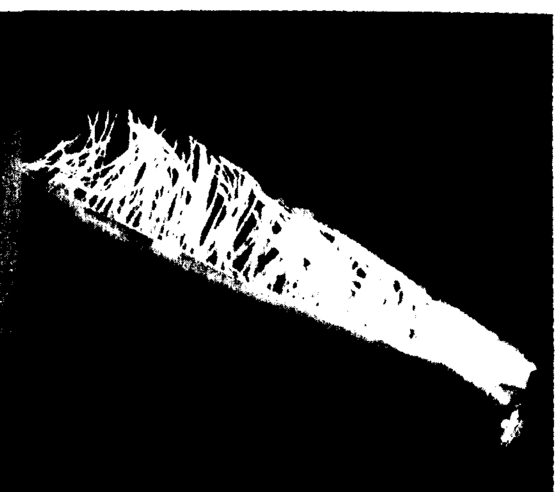


Fig. 18. *Isaria* Persoon ex Fries. (The growth on potato dextrose medium in glass tube – natural size).

One half of every kind of the mentioned sprayed samples was dried in closed Petri dishes at room temperature. The other half was kept in humid conditions most favourable for the growth of microorganisms. For this purpose 10 ml of distilled sterilized water was pipetted to the bottom of Petri dishes (under the tested sprayed samples); the dishes were closed and incubated at the temperature of 24–26°C.

After 3 days, samples dried at room temperature, as well as those maintained in humid atmosphere, were immersed for 3 or 5 minutes at 0.5 % or 1 % water solution of Hyamine 1622 or sodium salt of 4-chloro-3-cresol. Comparative samples were immersed in sterilized distilled water for 5 minutes.

All samples as well as those treated with biocides as with sterilized distilled water only, were placed in 100 mm Petri dishes on glass sticks and dried for 48 hours at room temperature. Then they were transferred to 100 mm Petri dishes on potato-dextrose agar medium prepared from 1000 ml of water extract of 200 g of sliced potato + 17 g of agar-agar + 20 g of glucose. The assessment was made after 10 days incubation at the temperature of 24–26°C and 90 % of relative humidity.

Results

In the course of our test with black-and-white photographic prints the following fungi were isolated and identified:

Acrostalagmus cinnabarinus Corda var. nana Oudemans (Fig. 9)
Alternaria tenuis Nees (Fig. 10)
Aspergillus amstelodami Thom and Church (Fig. 11)
Aspergillus candidus Link (Fig. 12)
Aspergillus flavus Link (Fig. 13)
Aspergillus fumigatus Fresenius
Aspergillus niger van Tieghem (Fig. 14)
Aspergillus terreus Thom (Fig. 15)
Chaetomium globosum Kunze (Fig. 16)
Chaetomium ochraceum Tschudy
Fusarium probably *oxysporum* Schlechtendahl (Fig. 17)
Isaria Persoon ex Fries (Fig. 18)
Paecilomyces varioti Bainier (Fig. 19)
Penicillium brevi-compactum Diercks (Fig. 20)
Penicillium sp.
Rhizopus sp.

Fig. 19. ***Paecilomyces varioti*** **Bainier (× 500).**

Fig. 20. ***Penicillium brevi-compactum*** **Diercks (× 250).**

Fig. 21. ***Scopulariopsis brevicaulis*** **Bainier (× 420).**

Fig. 22. ***Spicaria violacea*** **Abbott (× 500).**

Fig. 23. ***Trichoderma viride*** **Persoon ex Fries (× 500).**

Fig. 24. ***Trichothecium roseum*** **Link (× 250).**

Scopulariopsis brevicaulis Bainier (Fig. 21)
Spicaria violacea Abbott (Fig. 22)
Trichoderma album Preuss
Trichoderma viride Persoon ex Fries (Fig. 23)
Trichothecium roseum Link (Fig. 24)
and some species of *Streptomyces*.

The results of experiments on the protection of black-and-white photographic prints against microorganisms concern as well the dried samples as the ones incubated after spraying with sterilized distilled water, Greathouse, Klemme, Barker medium and/or a suspension of spores of fungi in Greathouse, Klemme, Barker medium. According to this data the growth of fungi was not observed on photographic samples and on the medium after a 3-minute period of immersion in 1 % water solution of Hyamine 1622 or 0.5 % water solution of sodium salt of 4-chloro-3-cresol. The immersion of photographic print samples in 0.5 % water solution even for as long as 5 minutes was not sufficient to destroy the microorganisms, which are able to vegetate on the surface of the sample. This was experimentally confirmed by the growth of fungi on potato-dextrose agar medium with samples, which were:

sprayed with sterilized distilled water, dried or maintained in conditions suitable for the vegetation of microflora, and then immersed during a 5-minute period in 0.5 % water solution of Hyamine 1622.

It is worth mentioning that the growth of fungi on the samples treated with 0.5 % water solution of Hyamine 1622 was much less than on comparison samples immersed in distilled water. On the basis of our experiments it may be concluded that black-and-white photographic prints can be protected against microflora, which develop on them, by immersing prints during 3 minutes in 1 % water solution of Hyamine 1622 or 0.5 % water solution of the sodium salt of 4-chloro-3-cresol. The solution should be prepared in distilled water.

General Remarks

Permanent record motion picture films and magnetic tapes must be made of slow burning cellulose esters or polyesters and processed in such a way that residual chemicals are reduced to a specific minimum, otherwise fading and staining of the image may occur with time.[49] If the containers of these records are not airtight, the air in the store-rooms shall be conditioned so as to maintain relative humidity of not less than 30 % or more than 40 % and it is recommended to maintain the temperature in the store-rooms at a level between

15–20°C.[9,18,23,37,38,49] It is worth mentioning that in high humidity and temperature microorganisms may cause not only the deterioration of audiovisual records but also outbreaks of mycosis and may favour toxin production especially in strong contaminated storage areas. The allergic response may be even immediate causing asthma or skin irritation and the numbers and types of fungus spores vary depending on the time of day, season, location, as well as humidity and temperature. Therefore disinfection of storage area of archives seems to be essential, where we have to do with the abundance of microflora. As proposed by us, 4-chloro-3-cresol has been utilized as fungicide and bacteriostatic agent in the following field of application: cellulosics, adhesives, collagenics, emulsion of film, paints. This compound is low toxic and is not hazardous for the environment, because it is degraded in sewage 24 hours after adaptation.

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Summaries

Part 1: Disinfection of contaminated motion picture films and magnetic tapes was carried out in sealed metal cans, having at the bottom and at the lid filter paper discs soaked with 2.5 % of 4-chloro-3-cresol dissolved in 96 % ethanol.

The contamination surface of audiovisual recordings may be cleaned with well-squeezed soft cloth moistened with 4-chloro-3-cresol dissolved in 96 % ethanol. The contaminated bobbins (spools or reels) may be treated in the same way. Disinfection of air in store rooms was carried out by using 1 or 2 % of 4-chloro-3-cresol in 96 % ethanol solution to the amount of 1 g of the microbiocide on m^3.

Part 2: Different species of fungi destroying black-and-white photographic prints were isolated and partly identified. Photographic prints can be protected against microflora by immersing prints for 3 minutes in 1 % water solution of Hyamine 1622 or 0.5 % water solution of sodium salt of 4-chloro-3-cresol.

The solutions should be prepared in distilled water.

1ère partie. La désinfection de films de projection cinématographique et de bandes magnétiques d'enregistrement présentant une contamination a été réalisée dans des boîtes métalliques scellées, sur le fond et sur le couvercle desquelles ont été disposés des disques de papier filtre imprégnés d'une solution à 2,5 % de 4-chloro-3-crésol dans l'alcool éthylique à 96 %.

Les traces de contamination en surface d'enregistrements audiovisuels peuvent être nettoyées à l'aide d'un chiffon doux imprégné d'une solution de 4-chloro-3-crésol dans l'alcool éthylique à 96 %, dont on exprime l'excédent de liquide. Les bobines et les rouleaux contaminés peuvent être traités de facon identique. La désinfection de l'air des locaux d'entreposage a été réalisée en utilisant une solution à 1 ou 2 % de 4-chloro-3-crésol à 96 % dans l'alcool éthylique, à raison de 1 g de solution microbiocide par m^3 de local.
2ème partie. Diverses espèces de moisissures responsables de l'endommagement des épreuves photographiques en noir et blanc ont pu être isolées et partiellement identifiées. Les épreuves photographiques peuvent être protégées contre l'action de la microflore par immersion, durant 3 minutes, dans une solution aqueuse à 1 % d'Hyamine 1622 ou à 0,5 % du sel de sodium du 4-chloro-3-crésol. Les solutions doivent être préparées à l'eau distillée.

Abschn. 1:
Die Desinfektion von verunreinigten Filmen und Magnetbändern wurde in verschlossenen Metallbehältern durchgeführt. Diese waren unten und am Deckel mit Filterpapierscheiben ausgestattet, die in 2,5 %iges 4-Chlor-3-Kresol, das in 96 %Äthanol gelöst war, getaucht worden waren.

Die verunreinigten Oberfläche von audiovisuellen Aufzeichnungen kann mit einem Tuch gereinigt werden, das in 4-Chlor-3-Kresol, gelöst in 96 % Äthanol, getaucht und gut gewrungen worden ist.

Die verunreinigten Spulen können auf die gleiche Art und Weise behandelt werden. Die Luft in Aufbewahrungsräumen wurde mit 1- bis 2 %igem 4-Chloro-3-Kresol in 96 %iger Äthanol-Lösung desinfiziert, und zwar 1 g Mikrobiozid pro m^3.
Abschn. 2:
Es wurden verschiedene Arten von Pilzen isoliert und teilweise identifiziert, die schwartz-weisse photographische Drucke zerstören. Die photographischen Drucke können gegen die Mikroflora geschützt werden, indem diese 3 Minuten lang in eine 1 %ige Wasserlösung von Hyamine 1622 oder eine 0,5 %ige Wasserlösung Natriumsalz 4-Chlor-3-Kresol getaucht werden. Zur Herstellung der Lösungen sollte destilliertes Wasser verwendet werden.

Die hauptsächlichen pilz- und bakterientötenden Mittel, die für Zellulose und Kollagen verwendet werden.

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