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ABSTRACT

Translated from its original German because of the great interest in mass deacidification in the United States, this report summarizes a substantial study of deacidification techniques conducted for the West German Library by the Battelle Institute. It begins with a summary of the findings of the study, which is followed by discussions of: (1) The Problem of "Acidic Books"; (2) The Development of Paper Production; (3) Aging Processes of Paper; (4) Approaches to Solutions (transfer onto microfilm and preservation in the original form); (5) Preservation of Large Numbers of Books through Mass Deacidification Procedures (the American diethyl zinc (DEZ) process, the Wei T'o magnesium carbonate process, the French magnesium methyl carbonate process, and others); and (6) Prospects for the Implementation of Mass Deacidification in the Federal Republic of Germany. Information on the availability of the full report in German is included. (8 references) (SD)

COMMISSION ON PRESERVATION AND ACCESS

REPORT

SEPTEMBER 1989

MASS DEACIDIFICATION PROCEDURES FOR LIBRARIES AND ARCHIVES: STATE OF DEVELOPMENT AND PERSPECTIVES FOR IMPLEMENTATION IN THE FEDERAL REPUBLIC OF GERMANY

Peter Schwerdt

This report is a translation of an article originally published in German, which summarizes a substantial study of deacidification techniques conducted by the Battelle Institute for the West German Library. The Commission has funded the article's translation and its distribution in the U.S. because of the great interest in mass deacidification, and to add to the knowledge base necessary to make investment decisions in this preservation technology. The original article written by Schwerdt, who is a co-author of the full Battelle Report, appeared in issue 36 (1989) 1 of *Zeitschrift für Bibliothekswesen und Bibliographie*. The full report will be available in German in early fall 1989 in an offprint from the same journal, under the title "Massenkonservierung für Bibliotheken und Archive", from Verlag Vittoria Klostermann GmbH, Frauenlobstrasse 22, D-6000 Frankfurt a.M. 90.

SUMMARY

Paper that has been industrially produced since the 19th century has been subject to severe aging and decomposition processes due to its acidic content. Collections of libraries and archives are threatened worldwide by paper decay. Because of capacity and cost limitations, filming of endangered collections as well as the transfer of information to other storage media cannot nearly fulfill the increasing need for preservation. From the viewpoint of libraries, the preservation of books in their original form by subsequent deacidification and alkaline buffering of the paper is the most desirable option. However, manual deacidification in a single-leaf process, which is a routine procedure for conservation specialists, is not feasible for bound material in large quantities. Promising mass conservation procedures are presently being tested in pilot plants in the United States, Canada, and France.

The procedure of the U.S. Library of Congress uses the gaseous, but problematic, reagent diethyl zinc. Because of special safety requirements, the procedure is technically very elaborate and can therefore be employed economically only in mass applications. After successful operation of a second pilot plant, plans are being developed for the construction of a large technical plant.

The Wei T'o procedure and its French version, which use magnesium methyl carbonate in an organic solvent, are technically less elaborate and can be operated in small and medium-sized decentralized plants, e.g., those connected to libraries or restoration workshops. However, the procedures must be further developed and improved in some aspects before they can be implemented, especially in the context of requirements for environmental protection.

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In a project conducted by the Deutsche Bibliothek in Frankfurt and the Battelle Institute, and financed by the West German Federal Minister for Research and Technology, the existing procedures were studied and evaluated in order to obtain a rationale for the implementation of mass deacidification in Germany.

II. The Problem of "Acidic Books"

The mission of libraries and archives traditionally has been to preserve knowledge handed down through the ages, to collect present-day information, and to disseminate it for future need. The scientific and cultural development of past centuries is unthinkable without written documentation on paper. However, institutions that preserve the written and printed knowledge of humanity and make it accessible to the public face a constantly mounting problem worldwide that has reached catastrophic dimensions today. The most recent collections are particularly threatened by decay. Millions of books, newspapers, manuscripts, drawings, maps, and other documents printed since the middle of the nineteenth century have already been lost or are so badly damaged that they can no longer be used.

The predominant reason for this decay is the lack of permanence of paper of the industrial era, quite apart from wear and tear through use, inexpert handling, and unfavorable storage conditions. The machine production introduced after the middle of the nineteenth century leaves traces of acid and acid-forming substances in the paper, causing in time the decomposition of the fiber structure and thus the loss of durability of the paper.

In the sixty largest libraries in the Federal Republic with a combined collection of approximately 100 million books, about 12 percent of the collections must be categorized as "no longer usable," according to preliminary calculations from a recent survey of the Deutsche Bibliotheksinstitut. The figures of the individual institutions vary according to type and age of the collections. Of the relatively recent collections of the Deutsche Bibliothek (from 1945 on), only 3 percent are severely damaged. In the Bayerische Staatsbibliothek, which owns extensive collections from the time after 1850, the extent of the damage did not become apparent until an inventory was taken: over 30 percent of the material must be considered unusable at this point.

There are, however, no official standards or regulations to evaluate the condition of a book. A book must be considered endangered when the corner of a page ruptures after being folded once. Libraries consider a further lending of such brittle books very hazardous, since even normal handling could endanger the material.

Although the losses and damages are extensive today, an end of the decomposition process is not in sight. On the contrary, librarians and restorers know that the damages will increase substantially. With increased paper production since the introduction of machine manufacturing, the long-term permanence of paper has consistently decreased, and more and more books from the recent past reach the limit of durability after fifty to eighty years.

III. The Development of Paper Production

Since its invention in China approximately 300 B.C., paper production changed very little until the middle of the nineteenth century. Bamboo, hemp, flax, linen, and cotton provided the fibers for traditionally made paper.

Paper was a hand-made, labor- and cost-intensive, expensive product, almost a luxury item, and was used predominantly for administrative purposes, official correspondence, archival documents, and, later on, for the printing of books. The low production capacities corresponded to the low demand of earlier times. The population figures and the standard of living were low, and few people could read and write. The low demand delayed the development of new production methods and alternative fiber sources until the late Renaissance.

Macintosh's 1799 invention of the chlorine bleaching procedure to lighten colored plant fibers considerably increased the availability of suitable fibers for paper production. With his invention of resin alum gluing of paper en masse, as described in 1806, Moritz F. Illig made it possible to turn away from the traditional procedure of subsequent gluing. This development furnished the basis for mechanized paper production.

The acceleration of scientific, technical, and cultural progress during the last century resulted, however, in such an increased demand for paper that the available procedures and raw materials no longer sufficed.

During his search for alternative fibers, F. C. Keller succeeded in 1844 in using wood as a cost-effective, freely available fiber source for paper production. His invention of wood pulp production was followed in 1854 by the development of chemical wood pulp production using the soda, sulphite, and sulphate process.

The use of acids in production procedures, as well as the use of alum (aluminum sulphate) for gluing paper, are the causes of the low permanence of industrially produced paper. The hydrolytic decomposition of the alum due to humidity is a slow process that results in the release of sulphate ions which form sulphuric acid and free hydrogen ions in the paper. The acidity in paper can, indeed, be in the range of pH 4-6, depending on composition and age. The formation of acids and, simultaneously, the aging of the paper are accelerated through unfavorable storage conditions, such as exceedingly high air temperature and humidity, variations of the room climate, and air pollution, which exposes the paper to sulphur dioxide and nitrogen oxide. In combination with water, these oxides form acids that build up in the paper.

IV. Aging Processes of Paper

While centuries-old and even millennia-old papers are still usable today in their original state, it is precisely the "modern" paper that discolors, becomes brittle, and loses its durability until it is unusable within a few decades.

The aging and decomposition of the paper is determined by numerous complex chemical and physical processes, in which hydrolytic and oxidative reactions overlap. The decisive factor in this process is the decomposition of the cellulose fiber structure through a diminishing degree of polymerization, i.e., the fiber length of the long-chain cellulose molecules.

Natural cellulose molecules show chain lengths of around 10,000 monomer units, while chemically prepared wood pulp has chains of only 1,000-2,000 units.[1] The durability loss of the paper becomes noticeable only below an average length of 500, but increases considerably below that level. At fiber lengths of less than 200 units, the paper is completely brittle.

The causes for the loss of durability of fibers can be roughly categorized as follows:

- hydrolysis under the influence of acids;
- oxidation with formation of carboxyl and carbonyl groups;
- formation of netting between cellulose molecules;
- microbiological damage; and
- mechanical wear and tear.

Oxidation and hydrolysis mutually influence each other: the auto-oxidation of cellulose takes place at room temperature; the acidic by-products of oxidation accelerate hydrolysis. The hydrolysis of the cellulose causes the formation of new low-molecular products, which in turn increase sensitivity to oxidation.

Industrially mass-produced paper is especially sensitive, since cellulose obtained from wood is less resistant to decomposition processes than, for example, the previously used cellulose obtained from cotton or linen.

V. Approaches to Solutions

Although the low quality of industrial papers was criticized at the beginning of our century and the problem of acidic decomposition has been known for a long time, the research endeavors of many countries have so far produced few solutions. Two principal approaches are used in libraries and archives in order to preserve the printed cultural heritage:

- transfer of texts onto other data carriers, e.g., microfilm or magnetic and optical storage media; and
- preservation of books in their original form.

Apart from these approaches, it is, of course, possible to reprint the documents. This subject will not be treated here in detail.

1. Transfer onto Microfilm

Microfilming represents a good method for the preservation of printed information, but it is time- and cost-intensive. The capacities available at present are clearly insufficient to film a considerable part of new acquisitions or of the endangered older collections.

The same is true for electronic filming and storage via modem data processing. It should be mentioned that even the films available today, as well as the expensive magnetic and optical storage systems, have a limited life span of only a few decades.

2. Preservation in the Original Form

Books not only contain information, but often represent art objects or documents of high cultural value, which cannot simply be replaced by a reproduction. From the point of view of a library, the preservation of the material in its original form is therefore desirable.

In the state-of-the-art restoration workshops of German libraries and archives, endangered books are masterfully restored and preserved in their original form. For a long time, wet chemical procedures have been used successfully for neutralizing acids in acidic papers. Hydroxides or carbonates of the alkaline earth metals magnesium and calcium are most often used. The alkaline baths cause a neutralization of the free acids, and excess alkali is deposited in the paper as a buffer in order to prevent future acid formation. These aqueous procedures show very good results in terms of deacidification and long-term effectiveness, but they have only been used for individual leaves.

The books must be taken apart before treatment; the pages are neutralized individually, dried, and subsequently rebound. The manual deacidification of books is limited to very small numbers because of the time involved, and does not present a solution for the preservation of entire collections, in view of the enormous extent of the damage.

In spite of the extreme urgency of the problem, the fundamental task of preventive mass conservation was approached in practice only recently in the Federal Republic of Germany.

VI. Preservation of Large Numbers of Books Through Mass Deacidification Procedures

A mass preservation procedure involves the following tasks:

- extension of the durability of paper and the life span of books by a considerable factor;
- possibility of treatment of the entire endangered collection and all new acquisitions as soon as possible in order to limit further damage; and
- assurance of technical feasibility at reasonable cost.

From these tasks, the following basic requirements are derived:

- scientifically proven knowledge of effectiveness;
- complete and lasting neutralization of all acids;
- deposit of a sufficient amount of an alkaline buffer;
- even quality and quantitative distribution, suitable to the various materials of the book (papers, bindings, writing materials and colors);
- treatment of bound material and all other formats; and
- sufficient developmental status, cost effectiveness, compatibility with the environment, and safety.

Aqueous procedures are not suitable for the treatment of bound material in very large numbers because of various side effects and the necessary time- and cost-intensive freeze-drying. In the United States, Canada, and France, experience has been gathered with various nonaqueous procedures; the studies of the Battelle Institute focus on these procedures. The existing pilot plants for the procedures described below were evaluated on site, so that the specific characteristics of the developments, with their advantages and disadvantages, were studied and discussed with the respective experts and people in charge.

1. The American Diethyl Zinc (DEZ) Process

As the largest library in the United States, the Library of Congress emphasized in its development of a preservation procedure the need for both a high capacity and compatibility with all book materials without preselection. In order to be able to treat the entire existing collection of fourteen million books (with approximately 350,000 new acquisitions each year) within a period of twenty years, its goal is an annual capacity of one million volumes.[2]

Approximately 97 percent of the entire collection has a pH value below seven and is therefore basically endangered. At present, approximately 25 percent of the books are considered to be damaged to such an extent that they should no longer be used. This number is increasing by approximately 77,000 unusable volumes per year.

The development of the DEZ-process started in the laboratory of the Library of Congress, with the first tests conducted in 1973. The process, which runs at low pressure in the gaseous phase, uses the metallo-organic compound diethyl-zinc (DEZ, chemical formula $Zn(C_2H5)2$). This compound neutralizes the acid in the paper while forming zinc sulfate and reacts with the humidity of the paper to form zinc oxide as a base buffer substance. Ethane gas forms as a by-product.

By using a gaseous substance, many side-effects damaging to paper, printing inks, bindings, and so forth, which could occur in processes employing aqueous or other liquid phases, are generally avoided. Thus, the time-consuming preselection and examination of the books to be treated is unnecessary.

The handling of DEZ is, however, problematic because of its high instability and volatility. It ignites spontaneously in air, reacts extremely violently with water, and decomposes at temperatures above 120°C.

In the past, several varying processes were tested on both smaller and larger quantities (up to 5,000 books per charge), with several setbacks. Cooperation with the National Aeronautics and Space Administration (NASA) ended in 1985 after a fire destroyed the first pilot plant at the Goddard Space Center near Washington, D.C. According to an analysis of the events, the cause for the failure of the project was mainly incompetence and a lack of supervision of the project by NASA and therefore insufficient setup and monitoring of the plant.[3]

Based on the experience gained from the first pilot project, the concept of the procedure and its safety was completely revised. In cooperation with the DEZ producer Texas Alkyls, who had more experience in handling this dangerous chemical substance, a second test plant for mass deacidification was built in Houston, Texas, in 1987. The plant, designed for the treatment of approximately three hundred books at a time, has been running without major problems since its inception; since then, numerous tests to check plant components and to optimize the process have been conducted.[4]

In principle, the DEZ process consists of three steps with approximately seventeen individual substeps:

1. Vacuum drying of books in the treatment chamber to a desired residual humidity content of approximately 0.5 percent of their weight, for a period of approximately twenty to thirty hours.

2. Treatment with gaseous DEZ over a period of six to eight hours.

3. Rehumidification with water vapor.

The entire time of treatment of a charge is approximately fifty hours.

The possible annua capacity of the treatment is basically limited by the time-consuming drying phase; therefore, a staggered operation of several treatment chambers is considered for future large-scale plants. In such a manner, optimal utilization of auxiliary systems, safety and control technology, specially trained personnel, and other functions would be achieved.

The U.S. large-scale plant is designed for an annual capacity of one million books; this size is also considered as the lower limit for economic viability. The construction and development costs are estimated at approximately U.S. $11 million, and the yearly operation costs at approximately U.S. $2.8 million.[2] These estimates would result in a unit cost of approximately U.S. $4.10 per book.

After successful completion of the test phase, which demonstrated the feasibility of the process, the Library of Congress started planning for the realization of the large-scale plant. Nevertheless, some questions, e.g., regarding the long-term effects of the zinc compounds on paper, remain unanswered.

2. The Wei T'o Magnesium Methyl Carbonate Process

The Wei T'o process (named after Wei T'o, an ancient Chinese God who protects paper and books against damage from fire, worms, and thieves), developed by Richard Smith at the University of Chicago, is a liquid-phase, nonaqueous process. It is based on the same principle as the single leaf deacidification. Wei T'o sprays are already used by many libraries.

The complex base compound magnesium methyl carbonate (MMC) is used in a methanol solution. It is combined with a liquid gas mixture, which functions as a carrier agent, in an approximate ratio of 1:10. The acids in the paper are neutralized when magnesium sulphates are formed; the excess reagent remains as a base buffer in the paper in the form of magnesium carbonate and hydroxide. The alkalinity of the treated paper ranges from pH 8.5 to pH 9.5.

The National Library of Canada in Ottawa has operated the first Wei T'o plant since 1981.[5] Although designed as a test plant and built at a low cost (total project: approximately U.S. $500,000), the plant treats approximately 20,000 books annually. For financial reasons, a large-scale plant with sufficient annual capacity has not been built in Canada. The ready-made neutralization solution is supplied by the manufacturer, Wei T'o Associates, Inc., and is sent back for recycling, a practice that results in high transportation costs.

Since the methanol of the solution is incompatible with some bindings, printing substances, and colors, the books to be treated must be preselected. Approximately 30 percent of the books are sorted out as unsuitable and excluded from treatment.

A twenty-four-hour, two-step drying of the books in warm air and vacuum dryers takes place prior to treatment, since the MMC would react undesirably with too much humidity and form gelatinous magnesium hydroxide. The books are soaked with the solution for thirty minutes in the treatment chamber, which has first been evacuated. After drainage of the solution, the books are dried for one hour; the solvent is partially recovered during this stage. In a climate-controlled chamber, the treated books are returned to normal environmental conditions. The recovered liquefied solvent is returned to the manufacturer for recycling.

The process shows a severe weak point during the phase of solvent recovery: too many chlorofluorocarbonates (CFCs) are released into the environment because of further evaporation from insufficiently dried books. The CFCs used as a solvent are considered to be one of the causes of damage to the ozone layer. For environmental protection, they must therefore be completely recovered.

The solvent losses that occur because of the design and operation of the Canadian plant are not acceptable. The manufacturer has announced, but has not yet achieved, improvements of the process and the use of other solvents.

The advantages, apart from the safety and non-toxicity of the substances employed, are the ease of monitoring and controlling the process and the comparatively low technical complexity. It therefore can be used for decentralized smaller and medium-sized plants connected to libraries, and can be operated within the framework of restoration workshops by in-house personnel.

The estimated investment costs for MMC plants are relatively low in comparison with those for the DEZ process; however, exact figures are not available. The total costs, including the operational costs, are estimated to be U.S. $3.50 to $6 per book at an annual capacity of 500,000 books.[2]

3. The French Magnesium Methyl Carbonate Process

Based on the Wei T'o process described above, France started its own deacidification testing and development in 1982.[6]

A regional office of the Bibliothèque Nationale in Sablé-sur Sarthe was chosen as the site for the pilot plant. Since 1975, all steps in book restoration have been conducted there, including filming, manual deacidification and strengthening in a single-leaf procedure, and rebinding. The books are sent from Paris for restoration, but are stored in Sablé after their restoration; only the films are returned to the Library. In the fall of 1987, a pilot plant for mass deacidification began operation in Sablé to test the practical application of the MMC process and to gain experience for the design of a large-scale plant.

The French operation differs little from the original Wei T'o process. The solution has, however, a slightly different composition still under development. The MMC solution, which is obtained from a British supplier, is mixed in the plant with the carrier agent Frigen R12 in an approximate ratio of 1:5.

From the beginning of the project, a recovery of the solvent after treatment and its re-use in the cycle after distillation was planned. However, this procedure, which is necessary for environmental protection and is also economical, does not yet work satisfactorily. The release of solvent residues from the treated books must be drastically reduced in the future. Problems are caused by the extreme cooling of the books to temperatures below -30°C during suctioning of the solvent vapors, which brings the further evaporation process almost to a standstill. After a certain period of time, drying is stopped. The residual solvent evaporates slowly into the environment after the books are taken out of the chamber.

The Battelle Institute study shows a need for further development, particularly in the areas of drying, where improvements can be made, e.g., with dielectric or microwave heating; solvent recovery and re-use; and device technology, process control, and operation.

Within the framework of the project, several books selected in Germany were treated in the French plant in order to test compatibility with various materials and writing substances. The quality of the treatment will be judged by chemical and physical paper analyses of some of the books.

4. Other Procedures

Apart from the above mass deacidification procedures, which are closest to practical industrial implementation, numerous other methods have been suggested during the last decades. Even today, work is in progress on combining as many advantages as possible in a simple and cost-effective procedure. Among the most promising developments is the Bookkeeper process (formerly the Koppers process), which works by depositing minute magnesium oxide particles in the books using a Frigen-113 solution. Practical experience in a test plant has not yet been obtained.[2]

Another method worth mentioning is the Interleaf VDP (Vapor Phase Deacidification) process, in which, under regular dry environmental conditions, crystalline cyclohexylamine carbonate is deposited in the book. This substance, however, evaporates in time and does not leave a permanent base buffer in the paper.[2]

VII. Prospects for the Implementation of Mass Deacidification in the Federal Republic of Germany

Based on today's knowledge, the nonaqueous MMC procedures seem to be usable for the purpose of mass preservation of acid-containing books, with certain acceptable restrictions. The experience and the results gained in Canada and in France are satisfactory, and their suitability to the needs of the libraries and archives of the Federal Republic of Germany is promising. Such a procedure could be available for testing in the Federal Republic of Germany within a short time, e.g., as an extension of the Deutsche Bibliothek in Frankfurt. Additional plants with treatment capacities of 100,000 to 500,000 books per year could later be operated individually in other libraries and archives.

In order to be used in Germany, the procedure must be further developed with respect to drying, solvent recovery, and operational aspects. Working in an environmentally safe manner with closed solvent cycles is possible according to the latest technology, as proven by the examples of chemical cleaning, metal degreasing, and extraction procedures. The search for alternative solvents also has to be continued, with the goal of avoiding the use of CFCs altogether.

The CFC producers, who have agreed to a medium-term suspension of the production of certain CFCs, can be expected to develop environmentally safe substitute materials. However, the toxicological safety of these materials must be tested, which could delay the availability of the substitutes considerably.[7]

The U.S. DEZ process is, in principle, the more elegant engineering solution. Because of its high technical expenditure, however, this process is economically feasible only for large capacities. The use of the DEZ process for mass deacidification in Germany is considered possible, provided that the plant is built by the present knowledgeable contractor on an existing chemical site and operated by trained technicians. For economic reasons, the plant capacity must reach the American volume of one million books per year.

So far, the premise has been that planning for a German DEZ plant could begin only after the U.S. large-scale plant was operating successfully. In the meantime, however, a much faster development is in the making: the Dutch chemical corporation AKZO, which acquired the DEZ technology by taking over the majority of Texas Alkyls in the beginning of 1988, expressed an interest in building the first European plant in the Federal Republic.[8]

It should be stressed that all mass deacidification processes developed so far result only in an extension of the remaining life expectancy of books at the time of treatment, depending on their condition. A restoration of the original durability of the paper is not achieved in this manner. The research conducted internationally toward this end has, as far as we know, not yet resulted in a mass procedure applicable in practice.

The preservation of endangered library and archival collections can be successful only through the use of a comprehensive concept that combines all presently known measures of preservation and accommodates the possibility of future expansion.

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