MASS DEACIDIFICATION:

AN INITIATIVE TO REFINE THE DIETHYL ZINC PROCESS

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Summary

In the summer of 1992, the U.S. Congress approved a Library of Congress (LC) Action Plan aimed at refining the diethyl zinc (DEZ) mass deacidification process and assisting in the development of other deacidification processes. This report deals with the DEZ phase of the two year initiative. It describes the progress achieved in this effort and recommends changes that should be considered in any future application of the DEZ process.

Background:

- At the end of the procurement effort to obtain mass deacidification services in 1991, the expert advisory panel concluded that the DEZ process showed the greatest promise for meeting the Library's technical requirements.

- However, this process also had some unacceptable flaws:

    - Odor in treated books
    - Iridescent rings on coated paper and covers and chemical attack on some book covers.
    - Adverse effect on adhesives and labels.

Objective of this project:

- Minimize these remaining problems in no more than 12 runs in Akzo's pilot plant in Houston, Texas.

The Developmental Effort:

- Cause of odor a mystery since known chemistry cannot explain it. Several possible sources of odor formation investigated:

    - Impurities in diethyl zinc and the nitrogen gas used in the process
    - Degradation products present in pape
    - Air leaks in chamber
    - Tight or loose packing of books
    - Amount of alkaline reserve
    - Temperature in DEZ vaporization chamber
    - Temperature in reaction chamber

- Series of experiments in the Akzo plant and in the laboratory undertaken systematically ruled out all other possibilities for odor formation except the two temperature parameters.
- Lowering of these temperatures significantly lowered the extent of odor formation.
- About 4500 treated books stored in a room with no air circulation did not give off a noticeable odor. By contrast, 500 books treated for the procurement effort exuded a distinct odor.
- Chemical interaction between book covers and DEZ was also reduced at lower operational temperatures.
- Chemical attack on adhesives was also decreased at lower temperatures.

Operational difficulties:

- Inefficient plant design does not allow DEZ vaporization temperatures under 110°F.
- Minor modification to plant needed but impossible because of Akzo's decision to shut down the plant.

Optimal performance of Akzo pilot plant:

- Last two runs (numbered 11 and 12) employed optimum conditions to produce the best treatment that the Akzo plant, with its inherent limitations, was capable of producing in a *consistent and reproducible manner*.
- Achieved alkaline reserve of 2 to 3% calcium carbonate equivalents (LC's minimum requirement is 1.5%).
- There were no iridescent rings on glossy papers or chemical attack on book covers.
- Odor level was minimal
- A management panel that examined books deacidified in these culminating runs found 98% of the covers and textblocks acceptable and 94% of the treated books to be free of unacceptable odors.

Conclusions:

- Odors and chemical attack on some book covers are caused by higher temperatures.
- Iridescent rings on coated papers and covers are eliminated by maintaining a high enough DEZ flow rate.
- Near-perfect treatment is achievable.
- Problems are resolvable with minor engineering changes.

DEZ Pros and Cons:

- Main advantages:

    - Inks do not run or bleed since no solvent employed. This would be an essential requirement for treatment of archival manuscripts, but printed inks in books are less vulnerable.
    - Can deposit high concentrations of alkaline reserve, extremely uniformly, regardless of the thickness or size of a book.
    - All types of papers, including coated and dense, supercalendered papers, are thoroughly treated.
    - Zinc oxide deposit in paper least likely to produce color shifts in inks and pigments since treated paper is almost at neutral point (pH barely above 7). Calcium and magnesium-based processes provide a much more basic (higher pH) environment and increase the possibility of color changes in images.
    - A mature process which has been studied extensively for effectiveness; also extensive toxicology data available.

- Disadvantages:

    - Pyrophoric nature of DEZ needs good engineering, good safety practice and constant maintenance.
    - A complex technology, for which engineers and other technical staff are needed 24 hours a day.
    - Plant must be situated away from the library. Therefore, books need to be transported to and from the plant.
    - Substantial capital outlay (5 to 10 millions) needed for a new plant.
    - Economies of scale can only be achieved by building a plant with a substantial production capacity, necessitating a large capital outlay.

Other assessments of DEZ technology:

- Harry Ransom Humanities Research Center of the University of Texas recently concluded that "... it is now clear that the process works well for archives and manuscript materials."

- The General State Archives of the Netherlands determined this year that, of three processes studied for them by the highly regarded TNO Centre for Paper and Board Research in the Netherlands, DEZ is best suited for the treatment of archival materials and manuscripts.
- Liénardy in *Restaurator* in 1994 (Vol. 15, No. 1, p.1) found DEZ and Bookkeeper to be the two most promising technologies among seven mass deacidification processes compared.

Future possibilities:

- Library needs to decide whether to invest heavily in a new DEZ plant at this time or to keep its options open for the future.
- Mass deacidification is a technology that has not yet matured to its fullest extent. Therefore, continue to encourage the development of such technologies.

Introduction

Deacidification processes are used to extend the life of books, manuscripts and other paper-based materials by neutralizing acids in paper and impregnating it with an alkaline reserve that will continue to protect it from acid-induced degradation in the future. Over the past two decades, the Library of Congress has been at the forefront of the development of deacidification processes that can be applied en masse to large collections. In its search for an ideal mass deacidification process, the Library invented and further developed the diethyl zinc (DEZ) gaseous process and also brought about key improvements in solvent-based, liquid phase processes. In the conservation science community, gaseous processes have traditionally been deemed to have a significant edge over liquid phase, solvent-based processes, mainly because they preclude any possibility of adverse effects on inks, dyes and colored pigments in manuscripts, color plates and book covers due to bleeding or softening of inks. The following quotation from the inventor of the Wei T'o liquid phase process (or a "liquified gas process") sums up the strong bias that existed for a gaseous mass deacidification process:

> "Many researchers dream of finding a fountain of youth. In search for deacidification methods, the fountain of youth seems to me to be a gaseous method of deacidification. A gaseous method would be ideal, absolutely ideal from every point of view, if it could be made to work."
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> -- Dr. Richard D. Smith in Canadian Library Journal, Vol. 36, 1979, p. 326.

It can be said with confidence now that the DEZ gas phase process works. Since the Akzo Chemicals (formerly Texas Alkyls) pilot plant began operation in December 1987, over 200 scientific and commercial batch runs to deacidify library books, maps manuscripts and other paper-based materials from domestic and international collections have been completed without any safety problems. Problems which persisted with this process until recently have been resolved as a result of the present initiative.

Background

Earlier gas phase deacidification processes employed alkaline chemicals that could be vaporized and deposited in paper, such as ammonia, morpholine, and cyclohexylamine carbonate (CHC). All of these chemicals suffered from the fact that they deposited an alkaline reserve that was not permanent, since whatever could be vaporized once would vaporize again over time. In addition, these chemicals constantly exude an odor which is not pleasant and can also present potential health hazards.

In the 1970's, the Library of Congress, with the encouragement of the U. S. Congress, launched a research program to identify methods to neutralize the acid in books that led to their embrittlement. This research by Dr. John Williams, Research Officer, and senior scientist George Kelly, laid the foundation for most of the current mass deacidification processes. They filed four patents for new processes. One of these patents, filed in 1975, was for the invention of a gas phase deacidification process using the chemical diethyl zinc. They described the process by which DEZ vapor rapidly penetrates the fibers in book papers, neutralizes the acids present, and deposits a uniform, stable alkaline reserve of zinc oxide to protect the paper from future acid damage. Laboratory scale experiments were followed by a few successful small-scale experiments at a GE facility.

Library scientists continued development of the DEZ process through the 1980's with the design, construction, and operation of scaled-up test facilities. Like most research projects that dare to chart unfamiliar ground, the DEZ research and development effort had its ups and downs. Twelve test runs carried out by Northrop Services, Inc. in a retrofitted space simulation chamber had established the promise of this process. A pilot plant was then constructed at NASA's Goddard Space Flight Center, in which the process was to be perfected. The worst setback came when a fire broke out as the new pilot plant equipment was being subjected to an operational test without any books in the chamber. Subsequent analysis of this incident showed it to be the result of pathetically poor engineering practice and design. Water reacts *vigorously* with DEZ, giving off zinc oxide, ethane (a flammable gas), and heat. The heat can cause ethane to catch fire, unless this reaction is carefully controlled by limiting the amounts of water and DEZ that are allowed to mix. In the incident at the Northrop Services facility at Goddard, water was pumped into a chamber in the belief that all DEZ had been pumped out. In fact, a few hundred pounds of DEZ had been pumped into the chamber. Material balance, a fundamental ingredient of chemical process operation, was entirely lacking. Not surprisingly, this incident raised great alarm, as well as opposition to the DEZ process and set its development back by several years.

The Library then turned to a manufacturer of diethyl zinc to design and safely operate a DEZ small scale test plant. The Commerce Department granted a license to Texas Alkyls (now Akzo Chemicals, Inc.) to promote commercial application of the DEZ process. In 1989, a small scale test facility was constructed at the Texas Alkyls plant in Deer Park, Texas, with a capacity for deacidifying up to 500 books in each treatment cycle. The engineering of the DEZ technology was successfully demonstrated in a series of 23 tests without any safety problems. However, the process appeared to have some persistent problems with the quality of the treatment. Nevertheless, the process had reached a state of maturity at which the Library felt that an acceptable product could be produced with proper operational procedures in place.

In 1989, Congress directed the Library to consider for its deacidification services all technologies that could safely and effectively meet its preservation needs, rather than confining its attention to the DEZ process alone. The Library issued in September 1990 a request for proposals from all firms interested in providing deacidification services to preserve the Library's collections. Based upon the findings of a board of technical experts and test results obtained from an independent testing lab, LC canceled the procurement in the fall of 1991. Though each of the three processes that were submitted for consideration slowed the rate of loss of strength in acid paper by at least 300% percent, two of the processes failed to meet one or more of LC's preservation requirements and each resulted in a variety of aesthetic damages or other problems in treated books.

Of the three processes evaluated by an expert panel, only Akzo's DEZ process met all of the preservation requirements specified in the procurement effort (neutralization of acids in paper, provision of a specified level of evenly distributed alkaline reserve for future protection, and extension of the life of paper). For this reason, and also because the advisory board determined that the DEZ process had the greatest potential at that time for being improved in the short term to meet the Library's requirements, LC proposed that Congress approve an initiative to minimize problems associated with DEZ treatment, such as distinctive odors in treated books and iridescent rings on book covers and coated paper stock.

The Library placed a notice in the Commerce Business Daily (CBD) in the summer of 1992 to inform interested parties of LC's intention to enter into a sole source contract with Akzo Chemicals for a research and development effort to refine the DEZ deacidification process. A contract was signed in December 1992 for 12 test runs at Akzo's Book Preservation Facility in Texas.

The DEZ Refinement Effort

Objective: The primary emphasis of the recent research and development initiative was on the elimination of objectionable odors in treated books and on minimizing visual damage, such as iridescent rings and chemical attack on some pyroxylin-coated book covers as well as rings on coated paper. An additional factor was the effect on adhesives used in bookbindings and in labels. The scope of this study was to extend to all types of papers, inks, book covers, and other materials. Process parameters during the drying, permeation, rehydration and post-treatment steps needed to be optimized so that library books could be deacidified in a consistent and reproducible manner, with an adequate alkaline reserve and without process-related damage.

The Technical Team: To obtain broad-based professional assistance with its DEZ refinement initiative, the Library assembled a multi-disciplinary team of consultants. They included scientists from academia, technical experts in chemical engineering and paper technology, and professionals from the library and conservation fields, who helped LC design this research and development program. Consultants and LC staff members who participated in this effort are listed in the *Appendix*.

Methodology: Consistent with the Library's earlier policy of not experimenting with its collections, all of the library books used in this project were expendable books from the Library's Exchange and Gift Division. As an aid in monitoring the effects of process variables from one experimental run to another, two types of test books were routinely included in all runs in the pilot plant. One of the books was a soft-covered book made by sewing together a 1-inch thickness of unprinted, alum-rosin-sized paper. This book was made to exclude any adhesives or other extraneous materials other than the paper itself and cotton thread. This is the "white test book" to which reference may be found occasionally in this report. The variation of alkaline reserve deposit among different experiments was routinely tracked by measurements on treated papers from this test book. The other Library test book, frequently referred to as the "blue test book" is constructed of a small variety of different papers that include newsprint, acidic alum-rosin-sized paper, an alkaline paper, a coated paper, supercalendered paper, and Whatman paper. The composition of this book is presented in the *Appendix*.

Potential Causes of Odor Formation: None of the known chemical reactions of DEZ leads to the formation of an odorous chemical. Therefore, any odor(s) that form must result from uncharacterized side-reaction(s). A logical path to solving this problem would be to analyze the volatile products from DEZ-treated paper. If the odor-causing chemical could be detected, then the chemical reaction that produces this chemical could be recognized, and hopefully, eliminated. This was exactly the approach employed in earlier work carried out by the Library well before the 1991 procurement process. The presence of several compounds in trace concentrations was discovered. However, none of the compounds accounted for the characteristic DEZ treatment odor, which persists for several months after treatment. Immediately after treatment, there was also a sweet alcoholic odor, much of which dissipated after the post-treatment step in which treated books were flushed with air for three days. Since none of the chemical compounds identified by GC-MS (gas chromatography coupled with mass spectrometry) has a smell resembling the "DEZ odor," the chemical that caused this odor must have been present in too small a concentration to be detected by the sensitive analytical means employed. Without a substantive clue, the process of deciphering the main cause of odor was reduced to sheer speculation.

In the present effort, two studies were commissioned to dig a little deeper, one at Colorado State University and the other at NIST. The latter suggested that the odor had to be an intrinsic part of the deacidification process with DEZ. The report was very logical. However, by the time this work was completed, the laboratory-scale deacidification at the Universities of Delaware and Houston were finding it impossible to develop an odor in DEZ-treated books. They were able to generate an odor later at higher temperatures.

The only other recourse that seemed to make sense was to compile all the different possibilities that could lead to odor formation and then eliminate them one by one. The following potential causes of odor were outlined as a result of a discussion among LC staff, LC consultants, and Akzo staff:

- Air leaks in the reaction chamber leading to the introduction of oxygen and carbon dioxide and subsequent development of odor-causing species.

- Impurities present in DEZ or in the nitrogen supply.

- Interaction of DEZ, or impurities, with paper itself, or with some paper chemicals, or with degradation products that are generally present in old books.

- Interaction of DEZ, or impurities, with adhesives or with some other component(s) present in book covers or binding materials (visible evidence existed of chemical attack on some book covering materials, as well as on some adhesives).

- Packing of books in the reaction chamber: tightly closed books appeared to produce higher odor levels. Conversely, loosely fitted materials, such as unbound manuscripts and pamphlets developed little or no odor.

- High alkaline reserve levels (above 0.8 percent calcium carbonate equivalents). LC's minimum requirement is 1.5 percent calcium carbonate equivalents.

- DEZ decomposition, leading to uncharacterized reactions caused by too high temperature levels inside the book and/or in the DEZ vaporization chamber.

A systematic experimental effort was undertaken to examine each of these hypotheses. The effort at the pilot plant level was supplemented with laboratory experiments carried out by consultants at the Universities of Houston, Delaware, and Colorado State.

The chronology of events in the next section of this report describes the progressive elimination of most of these possibilities. Finally, it was the laboratory experiments that established that it was only at higher operational temperatures that the deacidification treatment was accompanied by an odor. In fact, most of the laboratory-scale experiments, which were carried out at room temperature, were unsuccessful at reproducing the odor that had generally come to be associated with the DEZ deacidification treatment. The challenge from then on was to get Akzo to lower two key temperature levels, one for DEZ evaporation and the other for book temperature in the permeation step when DEZ reacts with moisture in paper to produce zinc oxide. At first, LC's request was turned down on the grounds that these changes would undermine the safety of the plant. To their credit, Akzo personnel reconsidered this issue and became more receptive to LC's proposal for lower temperature levels.

It was then discovered that the plant design would not allow the lowering of the DEZ vaporization temperature to desired levels. Attempts to lower the DEZ vapor temperature from the normal 120°F to 70°F in the treatment chamber required reducing the chamber pressure. The normal pressure of 35 Torr was lowered to about 15 Torr to prevent condensation of DEZ on the books during permeation. However, after several test runs at the lower pressure and temperature, the permeation cycle experienced DEZ flow upsets. An engineering analysis of the problem indicated that the lower pressures in the chamber and DEZ vaporizer piping caused higher vapor velocities. A resulting pressure drop in the piping increased the pressure in the upstream DEZ vaporizer, which in turn prevented vaporization of the DEZ at the lower target temperature. This caused flooding of the vaporizer and process upsets.

To stabilize the process at lower DEZ temperatures, the DEZ circulation rates had to be cut back until uneven book permeation treatment occurred. This problem could have been overcome by increasing the throughput of DEZ gas into the reaction chamber by adding a parallel supply pipe. This modification would have delayed operations by perhaps 2 to 3 months and would have cost $10,000 to $15,000. However, this option could not be entertained as Akzo had already decided to shut down the plant.

Several test runs conducted for the Library in 1993 demonstrated significant progress in addressing the issues of odor and occasional physical damage in some treated books. Then, on December 13, 1993, Akzo announced it had decided to shut down its Book Preservation Facility for business reasons effective at the end of the first quarter of 1994. This action signaled Akzo's assessment "of limited prospects for the adoption of DEZ in the near future." In letters to institutions with which it had contracts, Akzo reported this action was "despite our firm belief that [DEZ] represents the best available technology to address a need that is real and truly worldwide." (See the *Appendix*)

Following Akzo's announcement, the chemical company continued to cooperate with the Library to complete its proposed cycle of 12 DEZ test runs. After much trial and error, the last two runs (numbered 11 and 12) were accomplished under conditions which were not what LC had specified, though these runs provided the lowest temperatures that Akzo managers and engineers were confident of being able to repeat. Those two runs demonstrated that odors as well as the chemical attack observed on some covers and adhesives could be greatly reduced or even eliminated in the vast majority of books treated at lower book and DEZ temperatures, while still achieving a higher alkaline reserve.

Assessment of odor in treated books: Odor is one of those elusive perceptual qualities that means different things to different people, and possibly even to the same person at different times. Therefore, it was necessary to establish a dependable and reproducible methodology for the assessment of odor in library books treated in different test runs over several months. An odor panel comprised of three conservators was set up to evaluate odor in treated books by comparison against two DEZ-treated books from earlier Test Run 3, which established the baseline parameters. This procedure was modeled after TAPPI Test Method T483. It was challenging, and perhaps impractical, to try to establish objective odor protocols that applied consistently over time to books treated from one run to another. Objectivity may have been compromised by the fact that DEZ odor, even in control books, is fugitive by nature and, therefore, dissipates over time. The books against which the constant comparison was being made smelled less and less as they continued to be riffled repeatedly, with the possible result that the evaluation of books from each succeeding run grew progressively more demanding. In any future studies, an instrumental method that quantifies odor emission would be most desirable.

Assessment of acceptability of treated books: Another panel composed essentially of upper management was set up to determine the acceptability of treated books from one run to the next, by a purely subjective evaluation of any perceptible changes in the appearance of the covers and the textblock, as well as the formation of any odors. An average of ten managers examined and scored 30 to 50 books from Test Runs 4 through 12. The average scores are presented as a bar chart in the *Appendix*.

Project Chronology

The following table provides a chronologically arranged descriptive summary of the DEZ R&D initiative, describing briefly the objectives and results of the test runs and of the complementary laboratory research efforts.

Date	Activity and objective	Comments
1/12/93	Test Run 1: Establish whether odor will be generated in absence of inks, adhesives, covering materials and degradation products from aged paper.	Odor was generated in test books made of new paper (no degradation products) without any adhesives, book-covering materials, etc. Therefore, odor must be due to interaction of DEZ with book paper. Baseline operational parameters were established for future runs. Books treated uniformly, 1% alkaline reserve.
2/93	Initiate consultation contracts with Professors Klaus Theopold, University of Delaware, and David Hoffman, University of Houston, to carry out laboratory studies that would complement the pilot plant effort.	Parallel laboratory scale experimentation would attempt to comprehend the chemistry underlying the problem of odor formation.
2/20/93	Test Run 2: Establish whether degradation products in aged paper play any role in odor formation.	The same test books as used in Run 1 (no adhesives, inks, etc.) were used to fill the chamber, but these books were aged artificially for different aging periods. Established that degradation products in aged paper do not generate odor.
3/93 thru 5/93	Establish laboratory setups at Universities of Delaware and Houston to simulate the DEZ process in the Akzo pilot plant.	This laboratory scale work would complement the knowledge gained from test runs in the pilot plant and aid in determining the course of future test runs.

Date	Activity and objective	Comments
6/93 thru 9/93	Laboratory Experiments at Universities of Delaware and Houston: The objective of these experiments was to reproduce the odor effect encountered in the Akzo pilot plant, and then to attempt a solution.	Fifteen experiments were performed under a variety of conditions in an effort to reproduce the odor generated in the plant. These experiments failed to produce any odor, except for a mild odor after permeation at 140F (the highest temperature achieved in the pilot plant). Even this odor was so fleeting that very little of it was left by the time the treated books arrived at the Library inside sealed plastic bags. *These experiments definitively established that it was possible to deacidify books with DEZ without producing an odor.* Evidently, some different chemical reactions occur in the pilot plant than those that we were able to recreate in the laboratory. A significant possibility is that the higher DEZ evaporation temperature employed in the plant induces a small fraction of DEZ to decompose before it has a chance to react with paper. These unknown decomposition products exist only briefly to react through a different, uncharacterized chemical route to produce the odorous compounds. Since high odor levels are generally associated with noticeable chemical attack on book covers, these degradation products of DEZ must also react with other materials present in book bindings.
6/14/93	Test Run 3: Study effect of reduced permeation time. Longer permeation time increases the probability of undesirable reactions, besides extending treatment cost.	No adverse effects due to reduction in permeation time from 8 hours to 4 hours. Treatment was extremely uniform, but odor developed and chemical damage persisted on some covers, especially on blue test book covers. Alkaline reserve was still at the 1% level and would be kept there until all other issues had been resolved.
9/29/93	Test Run 4: This run went to great lengths to remove all volatile chemicals, including those present originally in the books, and others generated in different steps in the process. The book temperature during permeation was also reduced to 110F, as compared to 130F in Run 3 and 140F in Run 2. This was the lowest temperature Akzo would allow at this time from a safety standpoint.	Treated books had a noticeably reduced odor in comparison with previous test runs. An internal LC-management deacidification assessment panel evaluated a limited sample of these books and found the treatment to be acceptable.
7/93 thru 10/93	NIST study to investigate odor formation.	Employed available data to suggest plausible causes of odor formation. Concluded that odor may be intrinsic to the reaction of DEZ with a variety of chemical compounds in books and the treatment facility.

Date	Activity and objective	Comments
9/93 thru 10/93	Study by Prof. L. S. Hegedus at Colorado State University to analyze the odor causing chemicals.	Prof. Hegedus ascribed odor formation to reactions caused after decomposition of diethyl zinc, rather than by diethyl zinc itself. The chances of such a decomposition process would decrease as the DEZ and book temperatures in the permeation phase of the process are lowered.
11/10/93	Test Run 5: Attempted to reduce DEZ temperature in the evaporator to 75F. Too high a pressure in the evaporator condensed DEZ to a liquid, which stopped the flow of DEZ vapor to the chamber. DEZ temperature had to be stepped up to continue the permeation process. The rest of the run was conducted at conditions that were about the same as Run 4.	The attempt to lower DEZ was a good effort to push the system to the limit. Unfortunately this attempt did not succeed. Odor level was about the same as in Run 4. I*t became evident with this run that chemical damage on covers is also much reduced along with the odor as DEZ and book temperatures during the permeation process is in decreased.*
12/14/93	Test Run 6: This renewed attempt at reducing book temperature during the permeation step did not succeed, as the written instructions were misinterpreted by plant operators and permeation was completed at a higher temperature.	In spite of the higher DEZ temperature in the evaporator and high book temperature (140°F) during DEZ permeation, the treated books have been evaluated relatively favorably by the Conservation Office odor panel.
1/5/94	Test Run 7: This treatment was completed at a reduced temperature as desired. The book temperature ranged between 83 and 105°F.	*Books were uniformly treated at the lowest DEZ temperature attained thus far and had the lowest odor level yet experienced. Also, chemical damage to pyroxylin covers was noticeably absent.*
1/17/94	Test Run 8: Attempted to lower DEZ temperature below the level attained in Run 7. In addition, a higher alkaline reserve of 1.5 to 2.5% calcium carbonate equivalents was attempted. Runs 1 thru 7 incorporated alkaline reserves of 0.8 to 1.0% calcium carbonate equivalents.	Due to limitations in plant design, DEZ flow shut off at a temperature in the low eighties before permeation was completed. Nevertheless, *an alkaline reserve of 1.5 to 3.0% calcium carbonate equivalents was obtained at a low odor level*. The goal of achieving an acceptable product was viewed as a distinct possibility if the DEZ temperature could be kept around 90°F.

Date	Activity and objective	Comments
2/28/94	Test Run 9: Objective was to obtain a high level of alkaline reserve while maintaining low enough temperature conditions to minimize odor formation.	One and a half hours into permeation, the DEZ temperature in the vaporizer dropped to 70°F and the DEZ flow was curtailed. The temperature was then raised by an Akzo technician to 135°F, as compared with LC's objective of 90°F. As anticipated, odor level was high after the treatment. However, these books were lost in transit from Akzo to LC for several months. By the time they were received and evaluated, much of the odor had dissipated. The management panel found 91% of these books acceptable from an odor tolerance perspective, and 99% of the covers and textblocks were acceptable.
3/5/94	Test Run 10: Repeat process plan as proposed for Run 9, with relaxation to allow Akzo a maximum DEZ temperature of 100°F -- an allowance of 10°F, since they contend that they are working at the edge of the capability of the plant.	Akzo started permeation with DEZ temperature at 130°F -- 30° above the compromise upper limit, 50° above the desired upper limit. The temperature was progressively lowered to 100°F a few hours after the start. Most of the books in this run were made up of super-calendered paper, which has a much higher moisture content. Normal drying left too much moisture in the books, generating a lot of heat and giving much higher alkaline reserves (above 3 percent). Permeation time of 10 hours was not enough t o react with all of the moisture. Several books remained partially untreated. Higher book temperatures led to higher cover damage. Lower DEZ flow rate led to stagnant areas in the chamber and creation of iridescent patterns on book covers and coated paper.
3/30/94	Test Run 11: Repeat the Run 10 process plan.	Akzo operators conducted the run under conditions that defined an operational comfort zone with the DEZ temperature just above 100 degrees for most of the process. All books were uniformly treated. Alkaline reserves easily exceeded the Library's minimum requirement of 1.5 percent calcium carbonate equivalents. The management assessment panel rated 92% of the books to have acceptable odors; the ratings of acceptable covers and textblocks were 98.9% and 98.1% respectively.

Date	Activity and objective	Comments
4/2/94	Test Run 12: Repeat the Run 10 process plan.	Operational conditions were about the same as those in the previous run. The objective was to establish good repeatability under standardized conditions. The process was again completed smoothly at temperatures that were 20 to 30 degrees higher than desired, but the books were treated uniformly at an alkaline reserve level that exceeded the Library's minimum requirement. The management assessment panel rated 95.2% of the books to have acceptable odors, which is the best rating of all 12 runs. They rated 97.4% of the covers and 98.9% of the textblocks acceptable.
7/94	Final receipt of treated books.	
8/94	Conservator and management panels conclude assessments.	

Miscellaneous observations

Uniformity of Deposition of Zinc Oxide within Paper: Recent work reported by MacInnes and Barron (Journal of Materials Chemistry, v. 2, pp. 1049-1056, 1992) indicated that scanning electron microscopy (SEM) data showed that the zinc oxide deposited by the DEZ process in coated paper did not penetrate under the coating. This observation was contrary to SEM data that had been obtained by the Library during the earlier developmental work on the DEZ process. Further investigation was undertaken to resolve these conflicting sets of data. Ten different coated paper samples selected at random from more than 300 books treated in Run 4 were analyzed by SEM and X-ray microanalysis in LC's Research and Testing laboratories; further confirmation was obtained from John Koloski and James Bond at the Government Printing Office, who also mapped the distribution of zinc oxide across the edge of each of the ten papers. All of the papers subjected to these analyses, without exception, showed the zinc oxide to be deposited most uniformly throughout the paper matrix under the coating. This is, in fact, one of the best advantages that the DEZ process has to offer. *DEZ can penetrate through all kinds of paper, and through the thickest books, to deposit finely divided zinc oxide most uniformly.* It can do so, not only because it is a gas, but because it is attracted towards the bound water molecules dispersed evenly throughout the book mass and reacts with them to form zinc oxide, which constitutes the alkaline reserve.

Effect of DEZ Treatment on Photographic Materials: It is not surprising now and then to find microfiche attached inside a book cover. Also, one of the most significant problems in photographic preservation is the acid hydrolytic degradation of cellulose nitrate and acetate-based photographic film. The possibility of using a mass deacidification process for neutralizing the acids in large quantities of film appeared attractive.

A few samples of microfiche, microfilm and motion picture film were included in one of the test runs with DEZ. The results were disastrous. The films curled and shrank badly. The effect was much worse than what one would expect from only the drying of film. It is clear that any photographic film material would be lost if exposed to DEZ.

Optimization of the DEZ process: The resolution of the problems of odor and visual damage did not come about easily and even entirely satisfactorily, as is evident from the preceding account. At least four of the twelve runs were compromised due to stoppages induced by limitations in the plant design or its operation. As a result, it was not possible to extend this effort to optimization of the process to make it run more economically. In any case, since Akzo decided to close down this plant, its optimization would have been of limited value. It needs to be pointed out that there is plenty of room for cutting back on several steps in the process, especially in the nitrogen flushing before the permeation step. Nitrogen consumption, which was a significant part of the total operational cost, as well as process time could have been cut down significantly. The drying step also needed to be made more efficient by using a higher capacity pump and a wider bore tubing connection to the chamber -- improvements suggested by LC personnel soon after the plant had been built. However, Akzo management was not persuaded that such a plant modification would make a significant difference in the rate of drying of books. Another possibility was to introduce a pre-drying step in a separate chamber to save chamber operation time.

The drying step needed to be further standardized. Process conditions for this step needed to be correlated firmly with the weight of books to be treated. The drying conditions, used successfully in most of the runs, caused Test Run 10 to fail, because most of the books in this run were composed of supercalendered paper, which is much heavier and, therefore, has a significantly higher moisture content. The average drying conditions were inadequate for this run, with the result that too high an alkaline reserve was deposited on the outer margins (about 4 percent calcium carbonate equivalents), while the insides of the books remained untreated when permeation was stopped.

Advantages of the DEZ Technology

- It is a mature process with extensive processing and toxicology data developed and most process-related issues resolved at the Library's expense. Even with occasionally languid attention from Akzo management, the pilot plant worked in a problem-free fashion for 6 years without any significant problems.

- Even totally soluble inks will not run or bleed when papers containing them are treated with the gaseous diethyl zinc process. This feature makes this process invaluable for the treatment of archival materials and manuscripts, which are often written or annotated in soluble inks. However, the Library's mass deacidification program is focused primarily on books, where the danger of solubilization of printed inks by solvents is not as great. The ink solubilization problem in printed books is much more readily contained than with manuscript inks. A recent study, funded by the National Endowment for the Humanities and conducted by the Harry Ransom Humanities Research Center of the University of Texas, concluded that "...it is now clear that the process works well for archives and manuscript materials." The General State Archives of the Netherlands also determined this year that, of the three processes studied for them by a Dutch agency, DEZ is the best process for archival materials and manuscripts.

- The DEZ process can deposit high concentrations of alkaline reserve, *extremely uniformly, throughout all kinds of paper,* including coated and supercalendered paper, without any change in the feel or texture of paper.

- The final pH range of 7.5 - 7.8 is least likely to change the colors of inks and pigments in treated materials as compared with calcium and magnesium-based treatments, which give a final pH in the range of 9 to 10.5 pH units.

Disadvantages of the DEZ Technology

- Because of the pyrophoric nature of the chemical, a DEZ plant cannot be situated at or near library or archival buildings. Therefore, books and documents must be transported to and from the plant, thereby increasing the chance of damage to books and manuscripts and adding to treatment costs.

- An *essential requirement* for this process is a well- engineered and well-maintained plant that can manage the risks inherent in the process without any compromises. This requirement translates into relatively higher capital costs for plant start-up, as well as for operation and maintenance.

- Economies of scale can only be achieved by building a plant with a substantial treatment capacity, again necessitating a large capital investment.

Conclusions

Odors are caused by higher temperatures. It has been clearly established that there is a definite and proportional relationship between temperature levels to which DEZ is exposed in the vaporization chamber and in the main reaction chamber during the permeation step and the resulting odor level in treated books and the chemical attack on book covers, adhesives, and labels. The higher the temperature to which DEZ is exposed, the stronger are the odors and the chemical attack on book materials. These adverse effects can be minimized, and even eliminated, by promoting process conditions and plant design that minimize the heat to which DEZ is exposed. Books treated at ambient DEZ temperatures do not develop any odor. A logical possibility is that a small fraction of DEZ decomposes before it can react with the moisture in paper. The unknown products of this decomposition, which may well be transient in nature, lead to the formation of the odorous compounds, as well as the chemical attack on some book covers, labels, and coated papers.

It has also been established that tight or loose packing of books; the amount of alkaline reserve; reactions of DEZ with degradation products, unknown paper chemicals and adhesives; phases of the moon and the positions of various planets and constellations do not have any influence on the observed adverse effects of DEZ treatment.

Iridescent rings on coated paper and covers have been eliminated. Iridescent rings on reflective surfaces, such as smooth coated paper and book covers appear when the reaction between DEZ and moisture in these materials is a relatively static, diffusion-controlled process. This is a special case of well-established phenomena in gas-solid interactions, which lead to formation of products in concentric spheres when the penetration of the gas into the solid matrix is controlled mainly by diffusion. In the case of DEZ reaction with the moisture in paper, these concentric deposit patterns can be eliminated by maintaining a constant turbulence in the DEZ flow within the reaction chamber. The key parameter is the DEZ flow-rate. For the Akzo chamber, the minimum acceptable flow-rate was established at 150 pounds per hour. Higher flowrates are better, but DEZ flow into the chamber must be sacrificed to obtain lower vaporization temperatures. In spite of a satisfactory flow rate, if the permeation process is upset and comes to a standstill, even briefly, the formation of the iridescent ring pattern is unavoidable.

Problems are resolvable with minor engineering changes. It is believed that minor modifications in the plant could have been performed under normal circumstances to totally eliminate odor formation. However, Akzo's decision midway through this project to shut down the plant early in 1994 precluded any such initiative.

Near-perfect deacidification of books is achievable. Given the less-than-satisfactory circumstances under which the Library had to conduct a significant portion of this research and development initiative, it is heartening that the final two redundant test runs demonstrated that near- perfect results can be achieved by deacidifying books with the DEZ process, which is the only gas phase process known to leave a permanent alkaline reserve within paper.

Future of the DEZ Technology

The technology behind the DEZ process is now a tried and proven reality. It has been demonstrated to work well enough to meet all of the Library's requirements. It would be hard for any liquid phase, solvent-based process to match (1) the uniformity with which this process can deposit the alkaline reserve within even bulky, oversized books and within dense, supercalendered and coated paper, and (2) lack of any adverse effects on colored media. However, the utilization of this technology comes at a significant cost. These costs can be contained only with a significant capital investment in a large enough plant. If cheaper processes become available that are almost as good, safer, and probably more convenient, such costs may be hard to justify.

Since Akzo Chemicals' untimely decision to shut down the existing plant forecloses the Library's near-term ability to experience the efficiency of the DEZ technology at a large production capacity, and because of the high capitalization cost for a new DEZ plant, the Library will continue to assess the benefits offered by other promising, simpler, and cheaper deacidification technologies.

The Library's patents on the DEZ process expired in 1993 and 1994, and Akzo Chemicals terminated its DEZ license with the U.S. Commerce Department effective September 1994 (see Akzo's June 1994 letter in the Appendix). If any other institution or company in the U.S. or elsewhere decides to apply the DEZ technology to deacidification of library collections and archival materials, the Library will be pleased share the extensive technical expertise it has acquired in the development of this process.

TECHNICAL SUMMARY OF THE LIBRARY OF CONGRESS

DEZ BOOK DEACIDIFICATION PROCESS

RESEARCH AND DEVELOPMENT TESTS 1 to 12,

1993-1994

By George L. Eitel

Objectives of the Test Program

The principal factor affecting treated book odor that was learned during the laboratory experiments and the 12 tests conducted in 1993 and 1994 was the importance of controlling the temperature of the DEZ reactions during the permeation stage at temperatures below 100°F, where the treated book odors were found to be acceptable.

Following is a descriptive summary of the 12 Pilot Plant runs that were conducted during 1993 and 1994, plus tables graphically representing test data on the runs.

Overview of Test Runs 1-12

Twelve Pilot Plant test runs were designed by the Library of Congress to achieve the objectives described above and to learn more about fundamental relationships between the DEZ deacidification process and the quality of treated books. The first two runs utilized virgin white paper books, with duplicate operating conditions to eliminate potential effects of inks, paper quality, adhesives, and other foreign substances beyond the acidic paper. What was learned was that a temporary, sweet alcoholic odor developed, which disappeared after several months, while the characteristic industrial DEZ odor persisted, although it also decreased in intensity over the next 6 months.

Runs 3 through 7 were designed to lower the chemical reaction level to determine whether lower odors resulted in the treated books. The alkaline reserve was intentionally held in the 0.5 to 0.8% ZnO level, and permeation time was reduced from 10 hours to as low as 4 hours to minimize the exposure of DEZ to the cellulose to see whether lower odors were produced in treated books. As shown in the attached LOC Pilot Plant Run Data Summary, the alkaline reserves were within the target range, with odor ratings by conservators dropping from about 2.8 to 2.4 on a scale of 1 to 4, with 2.0 being the acceptable standard. Lower permeation reaction temperatures in Runs 4 through 7 may have helped improve the book odors, since independent research also showed that ambient temperatures (85°F) in laboratory experiments produced acceptable or no odors in treated papers. This lower temperature threshold became the target for improving odors in Runs 8 through 12. Also, the alkaline reserve level would be raised to about 1.5% ZnO to check out the impact of processing conditions on books at this more desirable level of buffering.

The goal in Runs 8 through 12 to keep book temperatures during DEZ permeation in the 100 to 105°F range was a function of the initial temperature of the books and the circulating DEZ vapors. Attempts to cool the DEZ to 90°F in Runs 5, 7, and 8 enabled Library and Akzo staffs to identify piping limitations that caused flooding of the DEZ vaporizer at circulation rates above 150 lbs/hr. The plant was designed for over 500 lbs/hr circulation at 25 Torr in the treatment chamber. However, the lower pressure of 15 Torr that is needed to prevent DEZ condensation in the chamber caused extra back pressure on the vaporizer to result in DEZ condensation in the vaporizer outlet unless close attention was paid to DEZ temperatures, pressures, and flow rates to enable the process to stabilize. Engineering assessments of this design limitation showed that future improvements to the Pilot Plant vaporizer outlet piping could eliminate this operating limitation. However, this option was precluded by the limited time available to complete the testing before Akzo permanently shut down the Pilot Plant.

By the completion of Run 12, stable permeation operations were achieved, and the ratings of the LC Management Mass Deacidification Assessment Panel reflected significant improvement of the treated book quality and odors to over 95% acceptance. The lower temperatures of DEZ circulation during permeation seemed directly correlated to the treated book lower odor levels. Another conclusion was that using the extra three days of post-treatment in the special chamber at Akzo significantly lowered the odor level of treated books. Concluding Run 12 was determined to be the best run of the series when looking at the whole process and book quality resulting from application of the DEZ technology. Sufficient understanding of potential process changes that could be employed to improve operability at the low odor conditions and to improve the plant capacity were identified for any possible future use in commercial application of the technology.

Details of each of the twelve runs in this series of optimization testing are presented below. Following also are operating results for all phases of each run, as well as special permeation data summaries.

Individual LC Test Run Summaries

Run No. 1 (January 1993)

This Pilot Plant test used plain, acidic paper books without inks, binders, or other non-cellulosic materials; and the treatment conditions were patterned after normal commercial runs at that time. The resulting level of alkaline reserve in the treated books was an average 1.2% zinc oxide. However, the book odors had a temporary sweet "alcohol" odor, which after several weeks vaporized and left the objectionable industrial "DEZ" odor that was persistent. The overall treatment time for this run was not the typical 60 hours, since a 42 hour downtime occurred during the drying stage when the vacuum pump failed and had to be replaced. No attempt was made until Run 8 to achieve the Library's specified alkaline reserve in DEZ-treated books, which is expressed as an average minimum of 1.5% in calcium carbonate equivalents. The zinc oxide alkaline reserves referred to in this technical report must be multiplied by 1.2 to convert them to calcium carbonate equivalents.

As planned, Run No. 1 would be followed by Run No. 2 to establish a base line with pure paper, from which future process variable adjustments could be made to evaluate improvements in book odor. Since laboratory testing has indicated that presence of air during permeation can cause sweet ethanol odors, future tests could be made after checking for air leaks at the start of the Pilot Plant operation. Attempts to remove the books from the chamber after permeation (but before rehydration) were not successful; it was hoped this could be achieved to identify odors in books before rehydration. Rapid moisture absorption within several minutes prevented determining whether odor formation occurred only during rehydration.

Run No. 2 (February 1994)

With plain paper books and operating conditions similar to those for Run No. 1, this test produced 1.2% zinc oxide alkaline reserve with the same temporary sweet alcohol smell that volatilized to the DEZ odor in several weeks. Zinc oxide distribution on the book pages was generally uniform. No book damage was observed during these two runs.

However, a pattern of unequal zinc oxide levels in the books was discovered, based on the book locations within the treatment chamber. A study of these patterns showed higher zinc oxide contents in the books located in the front of the chamber at the bottom of the stack. Engineering calculations indicated that the actual DEZ circulation rate during permeation was half of the design rate and that the vapor velocity through the distributor nozzles was insufficient to assure proper vapor flow to all books in the stack. This study showed that the desired DEZ circulation rates should be 400 to 550 lbs/hour, which would be tried in future tests. Another conclusion is that there was a bias between zinc oxide analyses performed by LC, the Swiss, and Akzo which needed investigation and resolution. Again, no system leak tests were conducted prior to the testing. Improvements to the water flow control during rehydration were recommended to Akzo by LC.

Run No. 3 (June 1993)

A review of the past 135 Pilot Plant runs was completed by LC. The conclusion was that Test No. 19 (conducted during 1989) should be used as a benchmark run because its specifications were typical of conditions needed to achieve significant reduction in DEZ permeation time and modified post-treatment conditions. The permeation time was reduced from 10 hours to 4 hours and the DEZ circulation rate increased from the normal 200 lbs/hour to 400 lbs/hour. The design circulation rate for the plant is about 550 lbs/hour. No DEZ circulation rate interruptions or problems were experienced at the 400 lbs/hour rate, which is different than what was experienced in later runs at lower temperatures. No coated or supercalendered paper was used during Run 3. Post rehydration processing included two steam stripping cycles (vacuum stripping of water followed by rehydration to 1% water). There were 382 treated books, of which 45 were pure white paper test books, 9 blue test books, 3 Akzo control books and 325 regular disposable library books.

Results of this test also showed temporary sweet alcohol odors followed by the DEZ odor. Alkaline reserve was 0.58% zinc oxide. Some book cover and spine damage was noted. About 20% of the books tested showed non-uniform treatment and zinc oxide distribution. A special LC member Odor Panel was formed to establish quantitative odor measurements of the treated books. Odor evaluations of the Run 3 treated books over three months showed a slow decrease in pure paper book "DEZ" odor and a slight increase in odors in regular books and in blue test books. This led to the conclusion that water rehydration might contribute to the odor forming reactions. Zinc oxide distribution in the treated book stack improved at the higher DEZ flow rates.

Recommendations were made to lower future DEZ reaction temperatures and increase the steam stripping and vacuum hold time during post-treatment to reduce odor production and attempt to strip the odors after they are created. Laboratory permeation experiments at room temperatures continued to produce no odors in the treated paper. By lowering the DEZ and treatment pressure from the normal 35 Torr to 15 Torr, the DEZ condensation point could safely be lowered below 70oF compared to the normal 115 to 130oF operating temperature in the Pilot Plant treatment chamber. Akzo was asked again to conduct a system check for air leakage in Run 4. The continued lower alkaline reserve target of about 0.6% zinc oxide was recommended for the next run, because this would require a lower level reaction and catalytic effect of the zinc oxide on potential odor forming reactions.

Run No. 4 (September 1993)

The objectives of Run 4 were focused on lowering the DEZ reaction temperature to reduce treated book odors. Laboratory experiments at DEZ reaction temperatures from 95 to 130°F produced paper odors. Accordingly, Akzo agreed to reduce operating DEZ temperatures to 110°F or lower, with book temperatures at 70°F. Maximum DEZ circulation rates were desired to improve the distribution of alkaline reserve treatment throughout the stack. Increased numbers of pulsed nitrogen purges and rehydration vacuum strip cycles were planned to remove any odorous volatiles produced in the processing. Representatives of the LC Technical Management Team attended Run No. 4 to assist in additional data gathering and analysis. Temperature profiles of all 18 book RTD's (resistive thermal devices) were taken every 15 minutes. There were 356 books treated, including 15 pure white paper books, 13 blue test books, 3 Akzo test books, and 325 disposable library books.

This run resulted in lower odor levels than in Run 3. The DEZ circulation rate of 500 lbs/hr and 70°F book temperature depleted the DEZ internal inventory and required a reduction to 120 lbs/hour to stabilize operations at a DEZ temperature of 102°F. Condensation of DEZ occurred in the chamber; 12 hours of full vacuum were required to purge the DEZ from the system. Analysis of the pressure/temperature profiles during the permeation cycle shows that the pressure during the first 45 minutes was not low enough to prevent condensation at 82°F. This indicated the need for closer control of the vacuum pressure.

However, the achievement of a lower DEZ temperature operation was most encouraging; and stability of operations seemed possible at a temperature around 90°. The alkaline reserve level was maintained at 0.6% zinc oxide. Since the permeation was not witnessed by technical representatives of Akzo or LC at the 3:00 a.m. timing, it was recommended that all future permeation operations should be scheduled to assure that such representatives could be present. Some special computer adjustments for the lower temperature ranges needed technical assistance for proper settings to enable the chamber operator to continue with the process.

Recommendations for Run 5 included medium DEZ circulation rates (300 lbs/hour) and 90°F DEZ temperature levels to lower the odor levels further. Other conditions were to remain the same. No special rehydration vacuum strips were recommended because the primary effort was to eliminate formation of odors, not to remove them at the end of treatment which could inhibit detection of actual odors being formed.

Run No. 5 (November 1993)

Objectives for Run 5 included improving the odor of the treated books by increasing the DEZ circulation rate to 300 lbs/hour and lowering the DEZ vaporizer outlet temperature to 75°F at a chamber pressure of 15 Torr during permeation. Akzo reviewed the temperature and pressure conditions to be certain that no DEZ would condense in the treatment chamber. The higher DEZ circulation rates were set to improve the DEZ circulation within the chamber and to produce even distribution of the alkaline reserve to all books in the stack. The lower DEZ temperature should reduce the odor levels in the books as seen in Run No. 4 and in the laboratory testing. The types of books to be treated were similar to Run No. 4, which had 15 pure white test books, 13 blue test books, 3 Akzo control books, and about 329 regular collection books. The alkaline reserve target was similar to Run 4 (in the range of 0.5 to 1% zinc oxide).

The average alkaline reserve was on target at 0.8% zinc oxide. Book odors were low, with averages slightly above the control book odors. The LC Management Panel of 10 persons rated 87% of the books to have acceptable odors. This same panel rated books treated in Run 4 to be 91.1% acceptable. Another 3 person LC Odor Panel (conservators) performed quantitative ratings, which indicated sweet "alcohol" and typical DEZ odors were detectable in most of these books up to 4 months after the run was completed, although the number of odorous books and the intensity of the odors decreased during this time. The odor ratings showed that post-treatment for about 4 days in a separate chamber with circulating air improved the short range and longer term odors of the treated books, compared to just rehydrating and returning the books to the Library.

Odor reductions did not meet the Run 5 target for several reasons: mainly because the stability of the process was interrupted three times with a stoppage of DEZ circulation. These interruptions required increasing the DEZ temperatures to as high as 112°F with an average of 94°F (which was better than in Run 4) and reducing the DEZ circulation rates to 200 lbs/hr to resume operations. These interruptions caused some rings of zinc oxide to deposit on the covers and some pages of books, although the LC Management Panel rated 96.5% of the covers and 98.2% of the textblocks as acceptable In Run 4 this panel rated 83.4% of the covers and 94.4% of the textblocks to be acceptable. The level of alkaline reserve varied within the stack of books as shown by the average zinc oxide of 0.9 % in the books located at the bottom, front of the chamber (near the door), while books in the top rear of the chamber were 0.7% and the bottom, rear locations had 0.8%. This bias had been reflected in earlier runs where the DEZ circulation was below 200 lbs/hr -- this causes laminar flow in the chamber distribution headers and poor DEZ distribution to the book stack.

Run 5 results indicated that operating controls during permeation still needed refinement and that the DEZ temperature had to be closer to 90°F to avoid flooding the DEZ vaporizer outlet piping. Unfortunately, the DEZ vaporizer had no pressure gage or level indicator to enable closer control by plant operators. The next run should aim to stabilize the DEZ circulation at about 200 lbs/hr and 90°F with a chamber pressure of 15 Torr or below. Post- permeation treatment would also be continued.

Run No. 6 (December 1993)

Run 6 objectives were specified to repeat the basic conditions employed in Run 5 -- 0.8% zinc oxide reserve, four hours permeation cycle, one rehydration cycle, and the same type of books. Permeation conditions were based on lessons learned in Run 5, which were to lower the DEZ circulation rate to 200 lbs/hr, to increase DEZ vaporizer temperature to 90°F, and to keep the chamber pressure at or below 15 Torr to prevent DEZ condensation in the vaporizer circuit. Stability of operation at a low temperature was the target for this run.

The odor levels of Run 6 books were better than in Run 5. The LC Management Panel rated 92.4% of the books acceptable for odor vs. 87.1% in Run 5. The 3 person LC conservator Odor Panel ratings were about the same as in Run 5 except for the post-treatment books, where the odors were better than the control books. One panel member rated the books after 3 months to be lower in alcohol smell, although the DEZ odors were slightly higher. The condition of book covers and textblocks was about the same as in Run 5. The alkaline reserve for Run 6 was 0.84% zinc oxide for the white books tested by LC and 0.68% for those tested by Akzo. The average Akzo test book alkaline reserve was 0.87%.

Operating conditions during dehydration and rehydration were similar to Run 5. However, the permeation temperatures and chamber pressure were higher than desired. The DEZ vaporizer temperature averaged about 115°F vs. the 90°F goal. The chamber operating pressure was 22 Torr instead of the 15 Torr goal because one of the three sets of inlet and outlet distributors was closed to improve DEZ distribution within the book stack. No DEZ flow upsets were encountered, and the process control was smooth.

The conclusion drawn from these results was that the distributors should be left open and the lower temperature effects should be evaluated during the next run, repeating target conditions similar to Run 6.

Run No. 7 (January 7, 1994)

The objective for Run No. 7 was to repeat Run No. 6 operating conditions, with all distributors open in the chamber to keep the operating pressure around 15 Torr, the DEZ vaporizer temperature around 90°F, and reduction of the DEZ circulation as needed for stable control of the permeation process. The quantity and types of books used were similar to those utilized in Runs 5 and 6.

This run did not meet desired target processing conditions. The main difference was that the DEZ vaporizer temperature was allowed to drop below 90°F, and at the end of the 4 hour permeation cycle the temperature was 75°F with a chamber pressure of about 12 Torr. With a 150 lb/hr DEZ circulation rate, the back-pressure on the vaporizer caused condensation. However, the process control was as good as could be expected, despite the absence of a pressure gauge at the DEZ vaporizer, which would have permitted fine tuning the control to prevent condensation. The alkaline reserve was 0.63% zinc oxide in the white test books, with a repeat of the bias of higher alkaline reserve levels in books located in the front, lower position of the chamber (0.82%) vs. the upper, rear locations (0.51%). It is believed that the lower DEZ circulation rate may have caused the distribution variance. The LC Management Panel rated the odors acceptable in 86.7% of the books evaluated. This is lower than in the previous run but agrees with the LC Odor Panel, which rated the non-post-treated books to have higher DEZ odors (a 3.4 rating measured against a 2.0 value of acceptability on the control books). Post-treatment improved these odors (1.97) to the level of the control books. The Management Panel determined that 99.1% of the covers and textblocks were acceptable.

With minimum book damage and the ability of post- treatment to lower the book odors to an acceptable level, the conditions suggested for Run 8 were the same as for Run 7, with a closer control of the DEZ vaporizer outlet temperature even if the circulation rate had to be decreased.

Run No. 8 (January 25, 1994)

The Run 8 operating conditions target was modified to obtain about 1.5% zinc oxide reserve and to control the DEZ permeation temperature to 90oF at a chamber pressure of 15 Torr to keep the odor levels low. This test would determine whether the level of alkaline reserve impacts on the odor levels in treated books. A series of drying model simulations was developed to set the new drying conditions for Run 8 at the higher alkaline reserve conditions (this utilized modeling developed for the Swiss Archives tests that were conducted at the Akzo facility). The numbers and composition of books to be treated were similar to Runs 5 to 7.

This run produced an average alkaline reserve of 1.45% zinc oxide, but the levels on each page of selected test books varied widely from 0.9% in the inner area to 2.2% in the outer edges of the paper. Uneven distribution of zinc oxide in the paper was visible with UV light. Two upsets in DEZ flow during permeation were experienced, which contributed to the uneven treatment. The DEZ flow stopped suddenly at the start of permeation and also at the 5.5 hour point of a planned 6 hour permeation cycle. Erroneous levels in the DEZ storage tank (T-903) contributed to the initial upset. The DEZ circulation rate was 150 lbs/hr. The non- uniform zinc oxide distribution on the pages may have resulted from the interruption of DEZ application and from the short permeation cycle time for this higher level of alkaline reserve. The permeation cycle and the dehydration hold cycle would be lengthened in the following run to improve zinc oxide distribution on the book pages.

The three-member Odor Panel rated books as having high odors after rehydration (2.36 rating on 55% of the books that had an alcohol smell, and 2.84 for DEZ odors in 93% of the books), with some improvement noted after post-treatment (1.95 rating with alcohol smells in 33% of the books, and 2.56 rating of DEZ odors in 100% of the books). Again, the control book odor standard against which ratings were made was 2.0. Rings of zinc oxide were evident on some book covers and pages. The LC Management Assessment Panel gave low ratings of acceptability to the books evaluated from this run -- 78.8% of the covers and 92.7% of the textblocks were acceptable. The odors of 87% of the books were acceptable, which is also a low rating.

Recommendations for the next run included extending the drying hold time from 16 hours to 20 hours and increasing permeation time from 6 hours to 12 hours.

Run No. 9 (February 28, 1994)

The objective of Run 9 was to demonstrate stable operation during high alkaline reserve (2%) book deacidification with low permeation temperatures of 90oF to generate low odor levels in treated books. The Swiss Archives drying model was used to predict drying conditions for this higher alkaline reserve test. Only one rehydration would be employed, to permit identification of the basic quality of these operating conditions. The DEZ circulation rate would be limited to about 100 lbs/hr to enhance stable operations.

Run 9 was partially successful. At the beginning of permeation, the DEZ tank was emptied due to a faulty weight indication in the T-903 tank, causing the DEZ flow to stop. Additional DEZ was added, and permeation was resumed after an 8 hour delay. About 1.5 hours into permeation at a 200 lbs/hr. circulation rate, the vaporizer evidently flooded as the temperature dropped to 70°F and the DEZ circulation stopped when the T-903 tank emptied. Akzo raised the DEZ temperature in the vaporizer from the 90°F goal to 135°F, which is known to be too hot to produce low odor books. The average book temperature was 120°F, which is about 20°F higher than demonstrated previously. Chamber pressure was controlled to about 17 Torr for the full 12 hours of the permeation cycle. Alkaline reserve was only 1% in the LC white test books and an average of 1.28 % in the Akzo test books.

Since the books treated in Run 9 had very high odors when they were removed from the Pilot Plant chamber, no further testing was conducted at that time. However, an LC Odor Panel evaluation of the books was conducted 5 months after the run, with odors of the books assessed as 2.43 against a control of 2.0. The LC Management Panel also rated the books and determined that 91.3% had an acceptable odor 5 months after treatment. Weathering of the treated books for 5 months had evidently significantly reduced the book odors. The LC Management Panel rated the covers and textblocks to be 98.9% and 98.5% acceptable, respectively.

Suggestions for the next run included repeating Run 9 conditions but reducing DEZ circulation to 100 lbs/hr. The key to low odor products still appeared to be lower permeation temperatures, and the challenge was to employ Pilot Plant operating conditions that would balance 90 to 95oF permeation temperatures against system design or equipment limitations. Akzo agreed to have its engineer present for the complete permeation cycle during additional runs, to provide specialized assistance in case any abnormalities occurred during the permeation step.

Run No. 10 (March 9, 1994)

This run was designed with Akzo to cool the books to 70úF then vaporize the DEZ at 90 to 100oF, with a low 100 lbs/hr DEZ flow rate. Previous experience continues to show these conditions are achievable if there is close technical monitoring. Conditions favoring 2% alkaline reserve were repeated from Runs 8 and 9.

Run 10 results, however, were not favorable. Poor quality treatment resulted from an unanticipated high percentage of books composed of supercalendered paper that Akzo loaded into the chamber. For this type of paper (which retains a higher moisture content than normal book paper), the operating conditions should have been adjusted to extend the periods of both the dehydration and permeation cycles. However, stable operations were achieved for the full 10 hours of permeation at 150 lbs/hr DEZ circulation, with 14 Torr pressure in the chamber, book temperatures from 80°F to 125°F, and DEZ vaporizer outlet temperatures down to 97°F. This was the first confirmation of stable operations for the full permeation period when striving for lower temperature permeation operations. Close technical operational monitoring seemed to be the key, although the impact of the type of paper being treated was not discerned until later when odor and condition evaluations were conducted.

Alkaline reserve levels measured by Akzo averaged 1.93% for multiple types of paper and 1.70 for white paper test books. LC analyses for its white paper test books averaged 1.63% zinc oxide, with a range from 1.25% in the top rows to 1.9% in the lower front area of the chamber. Low DEZ flows cause poorer distribution within the chamber. The LC Odor Panel average rating of the book odors was 2.85 compared to the 2.0 control standard. The LC Management Panel rated only 88.8% of the books to have an acceptable odor. The covers had a poor rating of 47.8 acceptance due to tackiness, rings, spotting, and other damage. The rating for the evaluated textblocks was also low at 83%, indicating non-uniform treatment. Higher peak book temperatures during permeation could have contributed to the poorer quality of treatment. It seems apparent that the high degree of supercalandered paper in the books was a major factor in the poor treatment results.

The remaining two runs (Nos. 11 and 12) before the Pilot Plant was permanently shut down in April would be targeted to confirm low odor capability of the DEZ deacidification process and/or to identify equipment changes needed to achieve processing conditions required to meet the target book qualities. Plans were made for a LC team of managers and contracted technical specialists to be on site to monitor these runs.

Run No. 11 (March 31, 1994)

The objective of Runs 11 and 12 was to conduct duplicate conditions in the testing to achieve 2% alkaline reserve with permeation targeted at a 90 to 100oF DEZ vaporizer temperature, 12 Torr pressure in the chamber, 100 lbs/hr DEZ circulation, rehydration twice with a water strip after the first rehydration cycle, followed by passivation at 15 Torr for the first thirty minutes of rehydration to minimize residual odors in the books. The traditionally used white and blue test books and other special samples would be removed for testing after rehydration so the 45 crates of books could be post-treated for 4 days in the special Akzo chamber. The goal was to finalize the baseline operation for acceptable book quality treatment. LC staff and a contract engineer were in attendance for both runs.

Results of Run No. 11 included a stable permeation operation with close technical support and monitoring. There were 399 books treated, weighing 799 pounds. Regular disposable library books numbered 368. Permeation operations were stable at 15 Torr in the chamber, with the DEZ vaporizer temperature starting at 113°F and decreasing steadily to 94°F over the 8.7 hour permeation cycle. DEZ circulation rates were held constant at 151 lbs/hr for the entire operation. Stable DEZ inventory was maintained. Two rehydration steps were accomplished with only 6 lbs. of total water being injected.

Akzo lab testing of the treated test books showed the white pages had 1.37% zinc oxide reserve, and the average of all types of paper in the test books was 1.55%. The LC Odor Panel rated the odors to be 3.13 on a standard of 2.0 as acceptable. The LC Management Deacidification Assessment Panel rated 92% of the books as acceptable 4 months after the run was completed. The ratings for acceptable covers and textblocks were 98.9 and 98.1, respectively.

Recommendations for the final run were to repeat most of the Run No. 11 conditions, with an attempt to lower the DEZ circulation temperature and book temperature each by 5 degrees.

Run No. 12 (April 4, 1994)

The objective of Run 12 was to duplicate Run 11 conditions, with the possibility of lowering the starting DEZ temperature another 5 degrees F to further lower the book odors.

Results of treating 402 books weighing 713 pounds included similar drying conditions, permeation operations with book temperatures 8 degrees lower than Run 11, steady DEZ circulation of 151 lbs/hr for 10 hours, chamber pressure of 14 Torr, and DEZ vaporizer temperatures that started at 110°F and decreased to 101°F. DEZ condenser temperatures were hotter than normal, which reportedly prevented lowering the DEZ vaporizer temperature to the mid-90's or lower.

The Akzo analyses of the their test books showed white paper to have 1.40% zinc oxide reserve and the average for all types of paper to be 1.62%. The LC Odor Panel evaluation of the books rated the odors at 2.73 at 1.3 months after treatment compared to a 2.0 standard odor control. The LC Management Panel rated 95.2% of the books to have acceptable odors, which was the best rating for all 12 tests in the series of runs. They rated 97.4% of the book covers and 98.9% of the textblocks as acceptable. These odor ratings could have been even better had the DEZ circulation temperature been lowered 5 to 10 degrees. This final test established an optimum target for meeting acceptable odor thresholds for any future facility design consideration. It is believed that Pilot Plant limitations could be readily solved by engineering design modifications for any future commercialization of the DEZ deacidification process

CONSERVATORS' REPORT ON THE

EFFECTS OF DEZ ON BOUND MATERIALS

By Martha-Lucia Sierra and Terry Wallis

The DEZ mass deacidification process has been tested extensively since its beginnings twenty years ago; the Library of Congress has focused testing primarily on bound volumes of non-rare collection materials. In the recent initiative to optimize the DEZ technology, a conservation team was responsible for coordinating, organizing, creating procedures and performing quality control for the 12 test runs, assembling and preparing book test materials, evaluating the materials after processing, and for interpreting and preparing written reports on the evaluation and test results. The group included a conservator in private practice, who was hired due to the size and complexity of the project.

Conservation Considerations/Examination of Treated Materials

From the conservation point of view, a successful mass deacidification procedure for non-rare collection materials is based upon physical and chemical as well as aesthetic considerations. Regarding the effect of the DEZ process on the stabilization of the object, the conservator can only evaluate the physical condition by visual examination. Ideally, this information would be used in conjunction with mechanical and chemical testing performed by a materials scientist. While physical and chemical stabilization can be measured in an objective way, aesthetic considerations are more subjective and are evaluated using olfactory, tactile, and visual criteria to determine the degree of acceptability of side effects resulting from treatment.

The aesthetic criteria originates from the conservator's orientation towards rare materials, but actually seeks to set a realistic base that may be applied to non-rare collection materials. For rare materials (not subject to mass deacidification), any damage caused by a process defines the treatment as unacceptable. The conservator will accept some level of alteration in non-rare materials, as a direct result of a mass treatment. However, the mass deacidification treatment should be non-invasive and non-altering, the "acceptable" change being minimal.

Visual examination of the object can be performed before and after the treatment with a checklist. The checklist will serve to confirm the before-treatment condition --for instance, that the binding appears unaffected; there are no dimensional distortions, stains, or non-uniform coloration of the covering material; no alteration or oozing of the adhesive at the head and tail of the spine; no lifting of original previously adhered materials; no iridescent rings on the covers, textblock and/or endpapers; no blocking, cockling, or warping of the textblock; and that the ink or other writing media is uniform, intact, and has not moved.

Physical handling will reveal any change in the feel of the covering material, distortion of the boards, swelling and/or cockling of the textblock, blisters in the plasticized paper covers or in labels, etc. The DEZ process can cause some materials to become friable as well as affect some types of adhesives, plastic book covers, and photographic materials. The mechanical examination, to be performed by a materials scientist, will assess any effects that the treatment process may have on the nature and longevity of the composite structure that comprises a book.

The olfactory criteria, like the tactile and visual ones, form part of the physical examination. Origin or cause and control of odor became one of the focal points of the investigation of the DEZ process. The conservation lab at the Library evaluated odors in books treated with DEZ, using the following criteria:

Since the test results varied due to the changes in the DEZ test runs specifications, odors in the books also changed. The Preservation Directorate compiled data from an Odor Panel, consisting of 3 conservators, who evaluated the smell of DEZ-processed books. Each member of the Odor Panel worked individually, using three control books to help in the verification of test odors. The panelists used two scales of odor for rating the DEZ-treated books against the control books: the first scale is the "intensity" scale, and the second one is the "descriptive" scale, which identifies different kinds of smells.

A second team of evaluators consisting of Library managers, comprised the Mass Deacidification Assessment Panel. They evaluated groups of 100 DEZ-processed books at a time, rating the physical condition and odor of the books. Once evaluations were completed, the processed books were shelved in a Library environment. Odor re-evaluations occurred at one and three month intervals after the first odor evaluation.

Results of the 12 Test Runs

Each run was evaluated to determine necessary changes in the specifications for subsequent test runs. The first two runs used virgin white paper books without covers, inks, adhesives, or other foreign substances. Resulting from these runs were a noticeable odor with a temporary sweet smell, which disappeared after the books had been aired at room temperature for several months, but leaving behind the classic DEZ odor, which also decreased in intensity with the passing of time.

In runs 3 through 5, the run specifications were altered in an effort to control odors in treated books. The permeation time was reduced from 10 hours to 4 hours to shorten the exposure of DEZ to the cellulose. In run 4, the books were separated in two batches: one batch would not receive post-treatment rehydration, while the second batch would. Odor was lower in the books that went through the post-treatment step.

DEZ treatment at room temperature (85°F) in laboratory research produced acceptable odors in treated materials. This lower temperature threshold became the target for improving the odors in treated books. Runs 8 though 12 aimed at lowering book and DEZ circulation temperatures to reduce odor and physical damage in treated books. In earlier runs, the DEZ process exhibited certain limitations -- it occasionally affected certain types of plastics, adhesives, artists' colors, book covers, photographic materials, copying processes and coated paper of the non-rare collection materials. By the end of the R&D initiative, however, stable permeation operations were achieved, and lower DEZ circulation temperatures during the permeation step appeared to result in lower odor levels and very little physical damage to treated books. Also, exposing the books to three days of post-treatment in a separate chamber lowered the odor level of the treated books. In review, Runs 11 and 12 were the most successful.

The conservators' general sense is that the majority of book types processed in these 12 runs pass visual examination, appearing to exhibit little or no damage resulting from DEZ treatment. The conservator odor panel found odors in treated books to be more pervasive and less acceptable than did the deacidification assessment panel that was comprised of LC managers.