

# Halting Untimely Book Ends

Two promising techniques are being developed to save our embrittling printed heritage



Not all volumes are prone to the ravages of acid. Those pictured here, for example, are not only of recent vintage, but are also printed on acid-free paper.

By JANET RALOFF

Rummaging through old paperbacks stashed in the back corner of a closet or basement, you run across a cherished title deserving a second reading. But its yellowed edges crumble as you riffle through pages that have taken on the color and texture of those crisp leaves that only a few months back littered lawns outside. What's happened?

Most books printed since the mid 19th century "contain the seeds of their own destruction," explains William J. Welsh, Deputy Librarian of Congress. He's referring to acids. Modern papermaking involves chemicals that over time break down into acids that embrittle paper. For the Library of Congress (LC), which acquires roughly 1,150 new books each working day, the problem of prematurely aging books is a grave one. In fact, Welsh charges, "destruction of the printed word"

by acid is "the greatest crisis facing scholarship today."

"We have some 800- and 900-year-old papers at the library that are in perfectly good shape," notes Peter Sparks, LC's Director of Preservation. By way of contrast, Welsh points out, a number of 1960-vintage paperbacks contain pages that will shatter under rough handling. In fact, the acid problem is a relatively recent development.

Prior to 1800, papermaking principles had essentially gone unchanged since their development in China roughly 2,000 years ago: rags of linen, cotton and other plant fibers were separated, processed and dried into tightly woven meshes, then dipped into a natural, gluey sizing. But a century ago the demand for paper exceeded the supply of rags, forcing papermakers to turn to wood pulp. Eventually, continuous papermaking techniques developed, heavily dependent upon the use of chemicals for breaking wood down into

pulp fibers and for bleaching those fibers to remove their chemically unstable lignin.

Today most paper is made from wood in complex chemical processes that include many bleaching stages. Though bleaching may introduce acids, its main purpose is to remove lignin, to whiten and to stabilize paper fibers. An alum-rosin sizing—originally used primarily to keep ink from "feathering," or spreading on paper—is the major source of acid. Cellulosic fibers, which form the basic structure for all papers, are flexible and strong due to their major component—long, chain-like cellulose molecules.

Papermaker's alum (aluminum sulfate) sizing begins to break down during papermaking through a process called hydrolysis; among its breakdown products is sulfuric acid. Even after the paper is bound in a book, the hydrolytic breakdown of alum continues until all alum is hydrolyzed. Acid produced in the process slowly attacks the paper's fibers, cleaving its cellulose chains into smaller and smaller fragments. This chain cutting weakens and embrittles paper.

According to Richard Smith, the developer of a paper-deacidification process being tested in Canada, between 75 and 95 percent of the deterioration in bleached, chemical-wood-pulp, fiber papers is caused by acid attack. The remainder primarily results from oxidative attack. More complex than acid-induced hydrolysis, oxidative attack leads not only to the tawny discoloration of paper, but also to accelerated acidification.

Lignin, a natural constituent of wood, is removed from the papers used in most books—in large part to whiten paper, but also to stabilize the product and to retard oxidative yellowing. (Newsprint and other forms of inexpensive groundwood and unbleached-fiber papers are especially prone to oxidative attack—induced by oxygen in the air—because of their high lignin content.)

Chemical bleaching in book-grade pulp paper to remove lignin actually strips away 40 to 50 percent of the original wood. "The removal of 40 to 50 percent of the physical structure will produce a large proportion of empty holes even when the paper fiber itself is compressed in the papermaking process," Smith notes. This opening up of the fibers renders them especially vulnerable to chemical degrada-

tion, he says, and helps explain why modern book paper is so prone to acid attack.

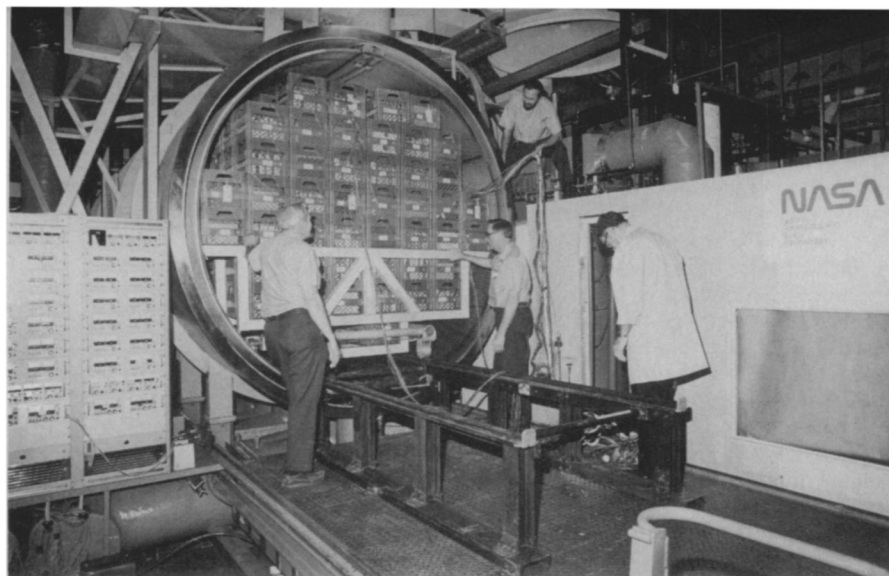
Although acidification can be halted, the damage it has already wrought cannot be restored. That's why LC and other libraries are intent on finding a technique that will allow them to treat new books—before acid-induced damage has occurred.

Since the 1960s, several acid-neutralizing processes have been developed. However, most of the more promising candidates are best suited for tackling only single sheets of paper. While rare-book conservators may find this adequate, it is costly. Labor charges alone for unbinding books, treating each page and then re-binding would bankrupt institutions like LC if instituted for routine processing of major collection holdings. That's what makes the idea of batch treatment so attractive.

LC's preservation office, which has spearheaded research on the deacidification of paper, is developing one process. Results from a recent test involving 5,000 volumes suggest that treating new books with the chemical diethyl zinc (DEZ) will double to quintuple the useful life of books. LC's vapor deacidification technology is the invention of two researchers now retired from the library's conservation division, George B. Kelly Jr. and John Williams. Patented in 1976, this process involves extremely reactive chemistry (DEZ ignites upon contact with water and oxygen), so treatment must be confined to a closed chamber. To ensure that a deacidification agent neutralizes all existing acid, the agent must make intimate contact with each page of paper. And because of its size (at 10 angstroms in length, 2 million DEZ molecules could rest on the surface of a pin), DEZ permeates even closed books easily.

An ordinary pressure cooker was used in the initial trial. When tests scaled up to 400 books, LC had to contract the services of a General Electric Space Center vacuum-chamber reactor in Valley Forge, Pa. For the most recent test, LC used a thermal vacuum chamber at the National Aeronautics and Space Administration's Goddard Space Flight Center.

The DEZ process involves four steps. First, books are dried to remove water over a two- or three-day period. (During LC's test at Goddard, between 600 and 800 pounds of water came out of the books—"a virtual rain forest," notes John Packard



For the Goddard tests, LC's books were packed 10 to a crate. The plastic milk crates were then stacked in NASA's highly instrumented thermal-vacuum chamber as shown.

of Northrop Services, who supervised the run.) It's essential that this water be removed, Sparks explains, or the DEZ would "decompose prematurely and eliminate too much heat." Once the books are dry and the oxygen has been removed, DEZ is introduced and left to diffuse through the books. DEZ molecules permeate the fibers of the paper, bonding with them or with water, which has been tied up in a low-energy chemical bond. The process generates ethane (which is pumped out of the reaction chamber). After three to five days, the reaction chamber is evacuated to extract any free DEZ for recycling. (Roughly 350 pounds of DEZ were absorbed in LC's 5,000-book test.) In the final stages, water is returned to the paper.

During the later stages of the process, DEZ molecules generate an alkaline residue of zinc oxycarbonate. "One of the interesting results of this molecular generation of an alkaline reserve," Sparks says, "is a uniform distribution of small particles of zinc oxycarbonate throughout the paper fibers." The residue is important, he points out, because any good deacidification technique "must leave an alkaline reserve of between two percent and three percent of the weight of the paper to neutralize future acidic products."

Though LC's batch processing of 5,000 books was completed in 13 days last October, a several-month analysis of how evenly DEZ permeated the books and whether it left unsightly residue was not begun until December. (Feedback has been enlisted from six other libraries whose books had been included in LC's 5,000-book run at Goddard.) Should the tests prove as positive as preliminary analysis indicates, Sparks says LC will be looking to open a deacidification facility in the Washington area by late 1985, capable of handling 15,000 to 20,000 books per batch. LC's aim, Sparks notes, is the capability of treating 500,000 books annually.

"If you want a gaseous deacidification process, then diethyl zinc is the best way to go," says Richard Smith, president of Wei T'o Associates in Matteson, Ill. "But if

you want to do something more than strict deacidification or if you want to treat your books inside your library, then you want to use another process." Not surprisingly, he suggests the Wei T'o process. "It works. It does a good job. And," Smith notes with obvious pride, "it's the only mass-deacidification process in operation in the entire world."

The pilot plant Smith designed to prove batch processing of Wei T'o deacidification has been in operation at the Public Archives of Canada in Ottawa since 1981. It employs chemistry Smith developed while a Ph.D. candidate at the University of Chicago, and has since patented. For more than a decade the process chemicals have been available to librarians and paper conservators through Smith's company—for single-page treatment. But successful scaleup of the process for batch treatment was only confirmed in the Ottawa facility, which now handles 150 books a day, three days a week. (The three-day schedule is a result of underdesigning book-dehydration capacity. The Public Archives recently ordered a second, larger drier, Smith says, which should make possible operation at the design capacity—roughly 5,000 volumes a week.)

Smith describes his chemistry as similar to the aqueous process originally developed at the National Archives and Records Service in Washington. "They use water as the solvent and make magnesium carbonate ( $MgCO_3$ ) soluble in it by adding carbon dioxide to the water to produce magnesium bicarbonate." Not only do immersed documents absorb enough  $MgCO_3$  to neutralize the existing acid, but also to provide an alkaline reserve of the buffering agent to fight off future acids.

In the Wei T'o process, organic solvents are used in place of water. "Paper not only gets wet and weak with water, but it also expands," explains Smith. "So you couldn't treat whole, bound books because the paper would swell and be difficult to wet." Smith's organic solvents—different chlorofluorocarbons, like Freon—wet paper without weakening or swelling it. To

these solvents he adds alcohols (ethanol or methanol) and the soluble, acid-neutralizing magnesium alkoxide.

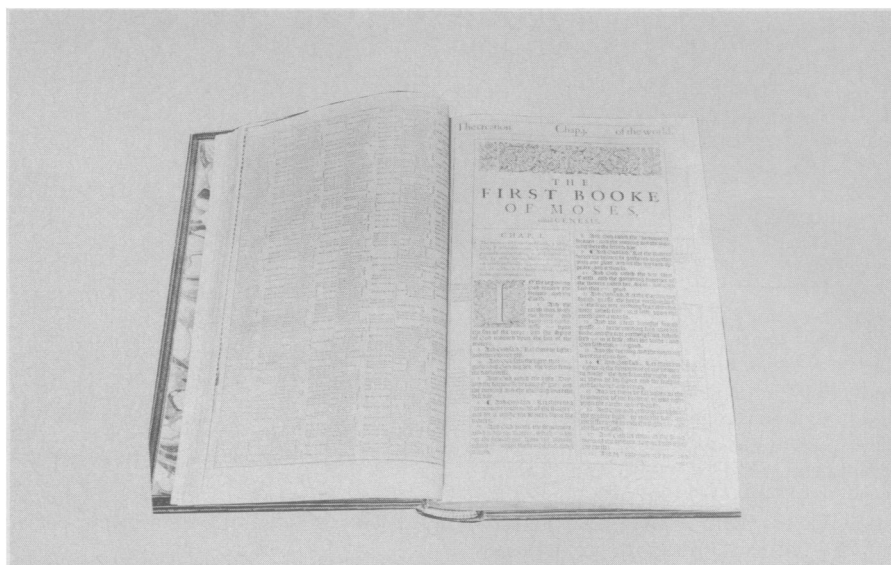
In contrast to LC's 10-day DEZ treatment, the Wei T'o process is speedy. Books dry for 36 hours. "After that," Smith says, "the entire treatment cycle takes less than an hour." Basketed books are taken directly from the vacuum dryer to the treatment chamber where air is removed, the treatment solution introduced, and the pressure elevated to 200 pounds per square inch. "After a few minutes," Smith says, the pressure is reduced, the solution surrounding books is drained away, and the books are flash dried. Much of the solvent remaining in the wetted books is recovered for recycling. (Remaining solvent is removed by a vacuum pump.) Once the chamber regains atmospheric pressure, books are removed and packed in cardboard boxes to "recondition"—regain room temperature and moisture—overnight.

"The reason I like my process is not particularly because I invented it," Smith says. "If we're talking about trying to make materials last longer, you have to do more than simply deacidify them; you've also got to protect them against other causes of deterioration and aging." He notes that magnesium ions in his chemistry tend to suppress oxidative reactions that might otherwise have been catalyzed by trace metals in the paper, such as copper, cobalt and iron. Those oxidative reactions are themselves one source of acid. Magnesium alkoxide will also catalyze the condensation of ethylene oxide onto paper, Smith says, to "retard oxidative attack and stretch out [a book's] life."

What's more, Smith says many papers have to be strengthened. "I demonstrated at [the University of] Chicago that acrylic resins can be dissolved in chlorofluorocarbons and impregnated in just the same way that deacidification agents are." And acknowledging that residues of the DEZ chemistry will inhibit subsequent attacks by fungus and other biological agents, Smith notes that addition of substances like bis (tri n-butyl tin) oxide to his chemical bath will achieve the same effects.

Cost and system safety may prove the factors deciding which batch-treatment technique a library ultimately chooses. "At the moment, the Public Archives of Canada estimates its costs [to deacidify books] at \$3 to \$4 per volume," Smith told SCIENCE NEWS. Sparks said LC "is shooting for" a per-volume cost of \$3 to \$5—"and it seems reasonable we can get to that." But the true commercial cost of either process can today only be "guesstimated," as both processes are still under refinement.

Regardless of what deacidification costs, most libraries will be unable to justify its use on every book entering their collections. "So we'll have to be highly selective," notes Welsh. And, LC's deputy librarian adds, "That's the most difficult problem we face." □



### Limiting acidification at home

Home libraries are as susceptible to embrittlement as their professional counterparts. But book conservators note there are several things home librarians can do to prolong the lives of their more valuable holdings.

First of all, not all papers are subject to the severe ravages of acid. Items printed on rag paper or on modern, but relatively expensive, alkaline paper (also known as "acid-free paper"), are generally immune. Library of Congress preservation director Peter Sparks says that eventually all printers will label volumes printed on acid-free stock. But today, to determine whether your most cherished volumes are undergoing acid attack, he suggests use of an "archivist's pen." Available through laboratory and library suppliers, these felt-tip pens dispense pH indicators; the color the pen's ink leaves behind denotes the paper's pH. Though quick, Sparks cautions the process is also dirty; testing leaves a permanent mark in the book.

If the book is not too far gone, you may consider it valuable enough to treat with chemicals ordered through those same library suppliers. One of them, Wei T'o, offers both solutions and aerosol sprays for dipping, spraying and brushing on neutralizing chemicals. But beware of the cost. Wei T'o president Richard Smith says materials costs for deacidifying a typical novel (having dimensions roughly 6 inches by 9 inches by 1 inch) with his chemicals could run between \$15 and \$30, depending on how efficiently one applied the chemicals. "And their benefit," he explains, "would be a doubling to quadrupling in the potential life of the book."

How long is that? Under ideal conditions, notes DEZ developer Henry Kelly, even a cellulose-based paper could outlast its owner. "If you really want to keep a book," he explains, "you should dry it out, wrap it in plastic and stick it in the deep freeze. At -20°F to -30°F they should last several thousand years," he told SCIENCE NEWS. However, since that's not practical, he notes a few ways to limit environmental deterioration.

As a rule of thumb, Kelly says "for every 10° rise in temperature, the rate of degradation doubles." But he adds that humidity complicates the equation; books last longer in dry environments. Smith has put together a table indicating how temperature and humidity affect book life (below). According to LC's deputy librarian, William Welsh, without special protection, most book paper produced in the past 50 years will last only 25 to 100 years.

So to store books at home, Kelly suggests one let books inhabit the same environment their owners prefer. Because it generally gets so hot in summer, the attic is the worst place to put books, he says. Owing to its humidity, the basement is the second worst. Since ultraviolet light promotes oxidative reactions in cellulosic paper, books should be kept away from windows and out of direct light. Finally, since atmospheric pollutants like sulfur dioxide and nitrous oxides are themselves acidic, windows should be kept closed to limit pollution-induced acid attack.

### Temperature, humidity and book life

| Average Temperature | Average Relative Humidity |       |       |       |
|---------------------|---------------------------|-------|-------|-------|
|                     | 70%                       | 50%   | 30%   | 10%   |
| 95°F                | 0.14                      | 0.19  | 0.30  | 0.68  |
| 86°F                | 0.32                      | 0.43  | 0.67  | 1.53  |
| 77°F                | 0.74                      | 1.00  | 1.56  | 3.57  |
| 68°F                | 1.76                      | 2.38  | 3.71  | 8.49  |
| 59°F                | 4.30                      | 5.81  | 9.05  | 20.70 |
| 50°F                | 11.10                     | 15.00 | 23.40 | 53.50 |

R. D. Smith/Library Science

*A life factor of 1 equals the deterioration that occurs in one year at 77°F and 50 percent relative humidity. A book's useful life would more than double by reducing temperature to 68°F, at 30 percent relative humidity it would increase 150 percent more.*