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New Ways Developed to Preserve Paper

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Of the nineteen million books and pamphlets in the Library of Congress, fully one third are too brittle to circulate to the public. At the New York City Public Library, the fraction is closer to one half. One recent study estimates that 97% of all the books published between 1900 and 1937 will have a useful life of fifty years or less--even though many books published in the Middle Ages are still in excellent condition.

These statistics underscore the urgency of a symposium on the preservation of paper and textiles, held at the American Chemical Society meeting in Washington, D.C. "It really hit about 1850," says symposium organizer John C. Williams of the Library of Congress Preservation Office.

Before that time, he explains, paper was made largely from cotton and flax by techniques that left it with a neutral pH--and sometimes with a reserve of buffering salt such as calcium carbonate. These are qualities now known to be ideal for durable paper.

But starting in the early nineteenth century, says Williams, the Fourdrinier papermaking machine came into widespread use. Production rapidly outstripped the supply of rags and forced the industry to turn to wood pulp, which yields cellulose of much lower molecular weight and durability than cotton. Papermakers also began bleaching the pulp with chlorine, which further degrades the fibers.

Worst of all, says Williams, was the choice of alum-precipitated rosin as a sizing, or waterproofing, agent compatible with the new machines. Without sizing, printing is impossible. Water-based inks blur and feather out on the sheet. But when that sheet is exposed to high humidity, the alum (aluminum sulfate) generates sulfate and free hydrogen ions.

Thus the pH of modern paper is between four and five. As soon as it is made, acid hydrolysis begins to destroy acetal linkages between the glucose subunits of cellulose. The result, says Williams, is modern paper that rapidly embrittles and disintegrates.

In an attempt to halt the self-destruction of their holdings, archivists over the years have subjected millions of documents to techniques such as silking, lamination, encapsulation, deacidification, and alkalinization. Sometimes, says Peter Waters of the Library of Congress Restoration Office, misguided attempts by one generation have complicated the problem facing subsequent generations. Contemporary archivists are in a better position to avoid such a legacy, he says, largely because they are better trained, are more aware of the problems, and have closer ties to scientists working on preservation.

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The ACS symposium was a portrait of what has become a nationwide preservation effort under the informal leadership of the Library of Congress. A number of presentations were devoted to basic research on the degradative process, covering such details as the catalytic role of trace metals, the influence of cellulose crystallinity, and the contribution of lignin's chromophoric systems to paper yellowing.

A second group of speakers described efforts to develop mass deacidification techniques, and one speaker predicted an industrywide shift to alkaline papermaking methods that could eliminate the problem for future generations.

Typical of modern deacidification research is the work on diethyl zinc described by Williams' colleague George B. Kelly, Jr. The process consists of drying the documents to essentially zero moisture content, exposing them to diethyl zinc vapor in the absence of air, and then destroying the excess diethyl zinc with alcohol. The paper rapidly regains its moisture when reexposed to air. The basic reaction is

$$(C_2H_5)_2Zn + 2RCOOH$$
$$(RCOO)_2Zn + 2C_2H_6$$

During three trial runs in 1978, 1210 books and 91 maps, all acidic, were subjected to the process in the giant vacuum chamber at General Electric's Space Center at Valley Forge, Pa. The results were encouraging. Treated books and maps were left with a pH of about 7.5, and no detrimental effects were noted on either the book bindings or the map colors.

Unfortunately, says Kelly, the treatment also left the documents more sensitive to degradation by ultraviolet light. When taken from the chamber they contained 1 to 3% zinc oxide. This compound serves as an alkaline buffer, but, like many other metal oxides, it reacts with atmospheric water vapor under the influence of UV, generating hydrogen peroxide and accelerating the degradation process it was supposed to stop.

In the original trials this effect was negated by adding a trace of iodide to the paper. More recently a better method has been found, says Kelly. At the very end of the run, carbon dioxide is admitted to the chamber, shifting the alkaline reserve from zinc oxide to zinc carbonate.

Although both Kelly and Williams regard the diethyl zinc process as one of the most promising deacidification treatments, they caution that it is not yet ready for mass production. The cost, for example, has been estimated at only $5.00 per volume, but this is still tentative pending further trials.

Furthermore, says Williams, diethyl zinc is very "bad stuff" to work with. It's pyrophoric in air and explosive in water. It must be handled by trained chemists. During the deacidification process, it must be contained within a tightly sealed vacuum autoclave. The technique is just not something that can be handled in an individual library.

Nothing would make librarians happier than to see the paper industry shift to a neutral or alkaline product, Williams says. Such paper would have the potential of lasting 1000 years. It's certainly possible to make alkaline paper and in fact to make it more cheaply, he says, but a combination of mental inertia and high conversion costs has kept the rosin-alum system on top.

But increasing shortages of raw materials may soon force a conversion, says Robert W. Hagemeyer of J. M. Huber Co., Norcross, Ga. The total world demand for paper and paperboard is expected to double by the year 2000, reaching 350 million to 450 million metric tons. At the same time, the cost of fiber and energy is expected to double, and the cost of water to triple, on a real-dollar basis.

Conversion to a neutral or alkaline sizing compound--Aquapel alkylketene dimers from Hercules, for example, or succinic anhydride from National Starch--lowers costs in two ways, says Hagemeyer. First, a mill's alkaline white water can be recirculated more often. Scale and corrosion problems, which in a rosin-alum system result from the buildup of alumina and sulfate ions, are sharply reduced.

Thus the need for makeup water is cut in half, he points out, with a corresponding savings in the energy needed to heat the water to process temperatures. Effluent volume also is reduced, and what does come out has the optimum pH for clarification and treatment.

Second, says Hagemeyer, a fiber web formed under alkaline conditions is 20 to 40% stronger than acid paper. Thus, without degrading the final products, manufacturers can reduce the content of expensive fiber and add more of a much cheaper filler used to give paper its whiteness and gloss. Furthermore, with alkaline papers papermakers can use calcium carbonate filler, which itself is cheaper than materials, like titanium dioxide, that are compatible with acid systems. Calcium carbonate has the added advantage of buffering the paper against acid city air.

Of course, all these economies take hold only after a plant is converted, says Hagemeyer. The conversion itself is hectic. The crews must be retrained. Sludge left in the equipment from the acid process causes spotting on the paper. "Any mill that is back to full efficiency in less than a year is doing very well," Hagemeyer says. Still, several large companies have converted and are happy with the results.

