"Making Book" On Permanent Paper

by John Cameron,
James River Corporation, Neenah, Wisconsin

For some time, there has been much concern about the durability of paper. In our public libraries, the paper in some books as little as 30 years old is so brittle that they cannot be handled. The major cause of deterioration in paper is acidification, from either an acid-based paper manufacturing process or from the reaction of the paper with atmospheric sulfur dioxide.

An estimated 77 million books in our research libraries, including 10 million unique titles, are affected by acidification. Because of the level of atmospheric contaminants in New York City, approximately 50 percent of the books in the New York Public Library are affected by brittle paper. Books printed before 1850 are less affected by acidification than books printed later. This article examines why this has occurred and what the future holds for the development and use of permanent paper.

Deterioration Of Paper

The rapid increase in population and literacy over the last 350 years greatly increased the demand for paper. Meeting this demand required many advances in traditional paper manufacturing processes, most of which decreased the durability of the paper. One of the most damaging changes was the use of papermaker's alum (aluminum sulfate) for sizing, flocculation, pH control and other applications.

Before 1800, books were printed on handmade paper produced from many different fibers, including flax. With the invention of the cotton gin in 1793, cotton gradually replaced flax as the principal papermaking fiber. The first successful use of wood fiber as a paper stock, in the form of groundwood, occurred in 1840. Wood fibers are shorter and weaker than the previously used natural fibers. But, because of its greater availability and lower cost, wood fiber replaced cotton and flax as the principal fiber used in paper.

To produce paper suitable for writing, raw stock must be treated with a sizing agent (hydrophobic material) to reduce its tendency to wet. If the paper is not treated, the ink will spread or feather, making the paper unsuitable for printing. Before 1800, paper was size treated by applying an animal glue-gelatine coating. In the early 1800's, an effective and inexpensive sizing process using rosin and papermaker's alum was developed. Instead of being applied as a coating, this was an internal size added to the pulp slurry. The alum lowered the pH of the pulp slurry, resulting in acidic paper. By 1850 the alum-rosin based sizing was widely practiced and paper was produced from a slurry of cellulosic fibers and other materials with a pH typically in the range of 4.5 to 5.0.

Chemistry Of Rosin And Alum Based Sizing

The rosin used in this process primarily consists of a mixture of several different tricyclic acids, which can be classified into two general structural types—pimaric and abietic (figure 1). The large cyclic structures shield the carboxyl group, resulting in considerable hydrophobic properties.

These rosin acids are essentially insoluble in water. Rosin size is produced by reacting rosin acid with an alkaline-water solution. Depending on the desired properties, from 5 to 80 percent of the rosin acid is neutralized. Rosin size is normally supplied to the papermill as a paste and is emulsified before being added to the pulp. In the sizing process, the rosin size and alum are added separately.

Papermaker's alum (hydrated aluminum sulfate) dissociates in water to form sulfate and hexahydrated, trivalent aluminum ions. The aluminum ions undergo a

Pepe Diniz, Collections of The New York Public Library

Photo Courtesy of the NY Public Library

Joining Forces in the Lion's Den

The advocacy movement for permanent paper is pulling together a unique coalition of authors, publishers, librarians, paper manufacturers, professional societies and government representatives. On March 7, many of these people gathered at the famed main branch of the New York Public Library for "Commitment Day."

The purpose of "Commitment Day" was to raise awareness of the need for book preservation. Lead by author Barbara Goldsmith, a group of noted writers, including Tom Wolfe, Joan Didion, John Gregory Dunne, Barbara Taylor Bradford, Nora Ephron, Judith Krantz, Kurt Vonnegut, Jr., Sidney Sheldon and William Safire, signed a declaration calling for the use of acid-free paper for all first printings of quality hard-cover trade books. Representatives from such publishing companies as Bantam/Doubleday/Dell, Harper & Row, McGraw-Hill, Random House, William Morrow, and Simon and Schuster, and literary agent Morton Janklow also signed the document.

The event brought to the forefront a campaign begun in earnest in the early 1980's. In August of 1984, the American National Standards Institute (ANSI) approved a new standard for the manufacture of permanent paper for printed library materials.

The movement really caught fire, however, in 1988. That year, the National Library of Medicine in Bethesda, Maryland, the largest health-science library in the world, created a Permanent Paper Task Force to encourage the increased use of acid-free paper for biomedical literature, and the Connecticut General Assembly became the first state legislature to adopt a resolution supporting the use of acid-free paper in the printing of all state publications. In October, Rhode Island Senator Claiborne Pell introduced a joint resolution to establish a national policy on permanent paper. That same month, the Technical Association of the Pulp and Paper Industry (TAPPI) sponsored the first conference to specifically address book preservation and the production of acid-free paper.

In addition to the groups mentioned above, acid-free paper has also won endorsements from the Association of American University Presses, the Association of American Publishers, and the American Library Association.

Books printed on acid-free paper that meets the ANSI standard can be identified by the infinity symbol inside a circle. It is usually placed on the copyright page, along with a statement of compliance.

For additional information on book preservation, contact the Conservation Division, New York Public Library, 42nd St. & 5th Ave., New York, NY 10018 ➾

series of hydrolysis reactions producing an acidic solution. Precipitation of the rosin proceeds through reaction of the anionic rosin and cationic hydrated aluminum. The products of this reaction are highly insoluble in water resulting in aggregation and precipitation of the rosin size particles. The presence of positively charged aluminum ions on the surface of the precipitated particles attracts these particles to the cellulose pulp, whose surface is negatively charged.

Alternative Sizing Agents

Cellulose is a polymer composed of glucose units with an oxygen linkage, referred to as a glycosidic bond, between the sugar molecules. Acid, even a very weak acid, will catalyze the hydrolysis of this glycosidic bond resulting in the degradation of the cellulose polymer. This degradation shortens the polymer and, if severe enough, will result in paper that is extremely brittle.

During the 1950's, sizing agents that react chemically with cellulosic fibers were developed. These materials do not depend on rosin and can be used under neutral or alkaline conditions. Because of the stronger chemical bonds formed and the better dispersion, these sizing agents are more effective than rosin-alum and effective sizing can be achieved with levels as low as 0.05 percent.

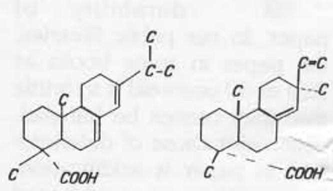
The two most commonly used synthetic sizing agents are alkylketene dimer (AKD) and alkenyl succinic anhydride (ASA). Alkylketene dimer reacts with the cellulose hydroxyl group to form an ester linkage (figure 2).

Alkylketene dimer is usually purchased as an emulsion, stabilized with a cationic starch. Although its efficiency does decrease, emulsified AKD, being fairly stable, will retain its ability to effectively size cellulose for a period up to two months.

The other reactive sizing agent, alkenyl succinic anhydride (ASA) (figure 3), is highly unstable and must be emulsified on site. ASA size is prepared by emulsifying alkenyl succinic anhydride with a polymer containing a cationic charge, usually cationic potato starch. The cationic charge serves to initially attach the size to the cellulosic surface. In the dryer section, ASA reacts with cellulose forming a strong chemical bond.

Alkaline Paper

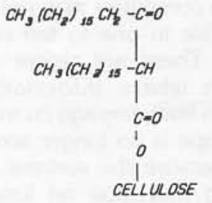
Alkaline papers are known to have a much longer life than acidic. Fortunately, there is a



ABIETIC ACID PIMARIC ACID

Figure 1

strong trend in the paper industry to convert from acid-based paper manufacturing (pH = 4.0 to 5.0) to the alkaline process (pH > 7.0). Currently, 30 percent of the U.S. free-sheet grades (paper not containing groundwood) are neutral or alkaline, and another 30 percent are being converted. The principal reason for this conversion is economics. The sheet produced in the alkaline system is stronger than that produced in the acid system, which permits higher usage of calcium carbonate and clay fillers. Since calcium carbonate is considerably less expensive than wood pulp, the furnish cost is reduced. In converting from the acid system to the alkaline system, the ash content of the paper can be increased from 7 to 12 percent to 18 to 25 percent. For a 500 tons per day mill, a 5 percent substitution of fillers for cel-



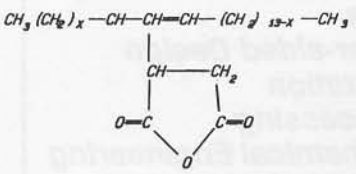
ALKYL KETENE DIMER (AKD)

Figure 2

lulosic fibers can result in a savings on fiber costs of $4 to 5 million per year.

There are two reasons for the increased strength of the alkaline sheet: first, cellulosic fibers are stronger and tend to form stronger bonds at higher pH levels, and second, less size (which may interfere with fiber bonding) is required in the alkaline process. Nearly all dry strength sheet measurements are increased in the alkaline system. This increase in sheet strength may be traded for higher levels of fillers or the substitution of lower cost fibers.

In addition to more permanent paper and a less expensive furnish, there are several other benefits to alkaline papermaking. One is pH control. Since the addition of calcium carbonate to the furnish will buffer the system at a pH near 7.8, it is not necessary



ALKENYL SUCCINIC ANHYDRIDE (ASA)

Figure 3

to use other methods to control the pH.

The alkaline process also offers increased paper machine life, increased production (provided the mill is not machine drive limited), and potential energy savings. The increased paper machine life is especially evident with system closure. In the acid system, the buildup of corrosive salt deposits can result in rapid corrosion. Machine corrosion is nearly eliminated with the conversion to the alkaline process. Since the sheet is stronger in the alkaline process, less stock refining is required. This reduced refining level results in the stock draining faster and having a higher solids content entering the dryers.

Since many of these advantages are trade-offs, it is unlikely that all of them will be realized. However, each mill can choose those that are most advantageous for its situation.

Converting From Acid To Alkaline Papermaking

Although equipment needs are critical in conversion from the acid process to the alkaline process, most of the effort required for this conversion is in changing operating procedures. New equipment that may be required include an emulsification system for sizing, and an on-site precipitator for calcium carbonate. Although emulsified AKD can be purchased, its efficiency begins to decrease immediately after emulsification. In some situations ASA is superior to AKD and its use requires an on-site emulsifier Precipitated calcium carbonate may be purchased, but, because of economics and quality control it is often desirable to produce it on-site. This is done by slaking burnt lime (calcium oxide) with water to form calcium hydroxide, and reacting the slaked lime with carbon dioxide to form calcium carbonate.

Significant operational changes are required for the conversion from acid to alkaline papermaking. Because of the high surface areas of the fines and fillers, a considerable amount of the sizing will be attached to these particles. If these particles are not retained, much of the sizing agent will be lost. In the alkaline system, it is necessary to optimize the retention sys-

Illustration by Lisa Hong

A Concern for the "Big Picture"

*by Jim Richard Wilson,
Ted Gallery,
Albany, New York*

Up until the mid-19th century, almost all paper used by artists was neutral in pH and made out of easily grown organic materials. With the explosion of trade with Japan came an influx of traditional asian papers made from stocks like rice and mulberry plants.

A flood of new pulp-based papers came after 1840, and artists, unaccustomed to worrying about durability, quickly adopted these plentiful, inexpensive papers. Many of the pastels and watercolors created by the Impressionists were executed on this stock.

The presentation of art work was also severely affected. The majority of framing materials for works on paper came to be made from inexpensive alum-rosin sized, pulp-based papers. The high acidity of these mat boards and backing boards had such a disastrous affect that by the latter half of this century, the majority of damage done to art work was attributed to framing.

The obvious deterioration of art caused by acidity has horrified artists and threatened important collections. Artists have learned to be more cautious in their choice of papers, and most major suppliers now list the pH of papers they offer. Manufacturers of framing materials have added alkaline buffers to their mat boards and undertaken extensive research into synthetic fibers that will remain neutral pH even when exposed to acids from outside sources. Collectors have become more aware of the importance of preservation as an active aspect of acquiring and maintaining their collections.

The outlook is very good as traditional and advanced neutral pH materials have become easily available, and methods for neutralizing acidity in existing art work are both advancing and becoming more accessible.

Jim Richard Wilson is an artist and art historian who serves as consultant curator to the Ted Gallery in Albany, NY, where our cover artist, Jim Zunk, frequently exhibits his work.

The paper industry is turning to alkaline processing as one method of ensuring our printed heritage doesn't self-destruct

tems such that a high level of the fines and fillers are retained on the first pass. Poor retention results in a very low level of sizing.

Another problem in conversion is the growth of slime deposits. Since alum has some biocide properties, slime deposits tend to be more of a problem with alkaline papermaking. These deposits can be controlled with the addition of a biocide such as chlorine dioxide.

Lastly, $CaCO_3$ particles may become entrapped in porous vacuum box covers and abrade the machine wire. This can be solved by reducing vacuum, replacing some of the calcium carbonate with clay or choosing vacuum box covers that are less porous. When dyed paper is desired, certain colors (especially yellows) require higher dye levels in alkaline papermaking than in acid papermaking.

The conversion from acid to alkaline presents many operational problems. However, solutions to these problems are known and conversion is occurring.

What Does The Future Hold For Permanent Paper?

As discussed, the paper industry is currently converting from acid to alkaline papermaking. Because cellulose is more stable at higher pH levels and because alkaline paper has the ability to buffer the acids from air pollution, books published in the future will be more permanent than those published in the last 150 years.

Although acidification is an important cause of book deterioration, it is not the only factor. Some lie simply in having library books available to the public. People tend to underline, tear out pages and in many ways abuse library books. Automated book handling systems are also very damaging to books. Therefore, regardless of the type of paper used, books will deteriorate. But, with alkaline paper, perhaps it will be at a slower rate.

A natural question to ask at this point is "With computer storage systems for information, why should anyone be concerned with the permanence of paper?" The problem with computer-based storage systems is that this technology is changing so fast that information stored in today's computers may not be accessible in one to ten centuries. There are recent examples where information stored a few years ago on magnetic tape is no longer accessible because the systems for reading that tape no longer exist.

Books remain the long term information storage system for our society and we should ensure that this information is available for future generations. A significant step in preserving books and other manuscripts is the ongoing conversion from acid to alkaline papermaking.

John Cameron is a research associate with the James River Corporation in Neenah, Wisconsin, and the 1989 chair of AIChE's Forest Products Division. He is a graduate of Michigan State University.