Paper and Other Writing Materials: Part II

Paper, a matted or felted sheet made primarily of cellulose fibers, is formed on a wire screen from water suspension. Due to its low cost and versatility, it has replaced many other materials in a variety of uses. Paper can be made with many specialized properties, some of the most desirable including high impact or tear strength, wet strength, resistance to water or water vapor, resistance to oil and grease, and resistance to flames.

Last month's Historical Note followed the development of writing materials used by early societies before the invention of paper. Some cultures used stone, clay bricks, wood, leaves, or bark to preserve their words and thoughts; others used the sheepskin (parchment), or calfskin or goatskin (vellum); the Egyptians laminated fibrous parts of the papyrus plant.

The Chinese created finely woven cloth on which they could paint calligraphic characters. Still others created felts by matting and intertwining animal hairs. These developments eventually led the Chinese to create true paper, in which vegetable fibers are "felted" together.

The oldest surviving samples of paper date from about A.D. 264, but the Chinese court official Ts'ai Lun reported his invention of papermaking to Emperor Ho-ti in A.D. 105. Ts'ai Lun used fibers from old rags, mulberry bark, fish nets, and hemp waste. The fibers had to be macerated or beaten until the individual filaments became separated; the fibers were then suspended in water and lifted out on a fine screen. The water drained through the screen, leaving a thin layer of tangled cellulose fibers which, when dried, formed a sheet of paper. The technique for forming paper has not been fundamentally altered in nearly 1,900 years.

The Chinese closely guarded their papermaking process, which remained a national secret for about 500 years, when the craft finally spread to Korea and Japan, brought by Buddhist monks who demonstrated how to make manuscript books from the bark of the paper mulberry tree. The Japanese made a thin, tough paper from a mountain plant called gampi; later they also used mitsumata bark and rice straw. The first block printing occurred in 770 in Japan, when the Empress Shotoku commissioned the printing of one million prayer papers; this job required six years to complete.

The art of papermaking reached the Arabs in 751, when their city of Samarkand in central Asia was attacked by the Chinese. The Arab governor managed to repel the invasion and, while pursuing the retreating Chinese army, captured prisoners, some of whom turned out to be papermakers. Samarkand had all the raw materials needed for the large-scale manufacture of paper: crops of flax and hemp and plenty of water. Baghdad began to produce paper in 793. Many 9th century Arabic manuscripts written on paper have been preserved.

The oldest surviving samples of paper date from about A.D. 264.

Paper was not manufactured in Europe until 1151, more than a thousand years after its first invention in China. The craft passed from Baghdad to Damascus, Egypt, Morocco, and finally reached the province of Valencia in Spain. A century later the Italians learned how to make paper. By the 14th century, France and Germany had also established paper mills.

Papermaking spread to North America by way of the Conquistadores, who set up a paper mill in Culhuacan, Mexico, in 1575. The first paper manufactured in what was to become the United States was established in Germantown, Pennsylvania in 1690. Canada's first paper mill, built in Quebec in 1803, produced paper for the *Montreal Gazette*. In these mills, each sheet was individually fabricated. A good worker could make about 750 sheets per day.

Úntil this time, most paper was made from linen or cotton rags. Rag paper is quite durable (cotton has a 91% cellulose content; linen, hemp, and jute vary from 60 to 90% cellulose). The rags were beaten by hand with a pestle or mallet until the fibers were separated. After 1680, automated beating machines simplified the chore.

The invention of the printing press in

1450 greatly increased the demand for paper. After about 1750 books were issued for the general public, newspapers and popular magazines had wide distributions and paper mills had difficulty meeting the demand. Nearly every magazine from 1775 on bore advertisements urging the public to "save your rags." Obviously, other materials had to be found.

Naturalist René Antoine Ferchault de Reaumur first suggested using wood as a papermaking material to the French Academy in 1719. After observing wasps make nests by chewing wood fiber, since they could make a paperlike material, he surmised men should be able to imitate the process. In 1730 Franz Brückmann printed a few copies of his geology book on paper made from the rock fiber, asbestos. About the same time, Flemish natural historian Albert Seba suggested using seaweed. In 1741 Jean Etienne Guettard offered swamp moss as an alternative. Other possibilities, used to varying degrees of success, include straw pulp, bagasse (sugarcane residue), Mediterranean esparto grass, and crushed bamboo. The most thorough investigation, though, appeared in six volumes between 1765 and 1771, when the clergyman Jacob Christian Schäffer in Germany made specimens of paper from 80 vegetable substances he found near his home. His six volumes included paper samples made of Indian corn husks, pine cones, potatoes, old shingles, reeds, leaves from various trees and plants, wasps nests, moss, vines, hemp, straw, cabbage stalks, asbestos, thistles, burdock stalks, cattails, and turf.

In 1800 Matthias Koops published a book in England on papers made from straw, deinked paper, and wood pulp. This publication marked the first use of wood pulp for practical paper production. In 1841 Charles Fenerty of Nova Scotia manufactured the first groundwood paper, using a mechanical process to crush wood into usable fibers.

The first chemical process for digesting wood pulp was discovered a decade later by Hugh Burgess and Charles Watt, who cooked wood chips in a solution of caustic soda. In 1857 Benjamin C. Tilghman discovered the "sulfite process," which used sulfurous acid (H_2SO_3) and wood chips, under high temperature and pressure, with the addition of a base such as calcium to prevent burned batches. Tilghman received a patent for his process in 1867, and it became widely used in the following decade, surviving until the 1940s.

In 1884 in Ğermany, Carl F. Dahl developed the sulfate pulping process, which used sodium sulfate instead of soda ash to produce a stronger pulp. The popular name for this was the "kraft process," from the German word for strong. The kraft process has become the dominant pulping method in paper manufacture. It is faster than other processes and is also practical with a wide range of wood species, though it yields a very dark-colored pulp. Not until the 1930s was an effective bleaching process found to turn kraft pulp into white paper. Other paper bleaching methods had used chlorine since its discovery in 1774. Calcium and sodium hypochlorites were also used for bleaching paper stock after 1800.

Softwood pulp fibers are 0.12 to 0.2 inches long, while hardwood fibers are only 0.04 inches. Fiber diameters vary between 0.0008 to 0.0012 inch. The longer softwood fibers give the paper strength and tear resistance, while the shorter hardwood fibers increase the smoothness and opacity of the sheet. The strength and durability of the finished paper is determined by the fibers and the formation and structure of the sheet. Natural cellulose fibers show no decrease in strength when they are wet, although the paper assembly may lose strength as the fibers float apart.

Paper is distinguished by several hundred different grades according to differences in material properties, raw materials, or manufacturing processes. The "basis weight" of paper, or weight per unit area, is measured in reams (commonly 500 sheets). A ream of "16 pound paper" weighs 16 pounds for standard 8 $1/2 \times 11$ inch paper. Paper is also measured by its thickness and density, and it is segregated according to gloss, opacity, brightness, and color.

 ${f T}$ he material properties of paper can be improved for specific uses. Since paper composed only of cellulosic fibers is water absorbent, water-based inks penetrate and spread across it, making printing and calligraphy difficult. Early paper makers learned how to impregnate the paper with various substances to hinder wetting; this process is called "sizing." The Chinese used starch for sizing as early as 768. By about 1337, other manufacturers used animal glues and gelatins and vegetable gums. In 1807, Moritz Friedrich Illig published his discovery in Germany that paper could be sized in vats with rosin and alum, though it took another 25 years before anyone put the method to practical use.

In the 19th century, papers began to be coated to provide special surfaces for fine printing. A mixture of white clay, casein or other adhesive, and dyes (if desired) was spread on the surface to fill the small irregularities caused by non-uniform fiber size or uneven distribution across the mesh screen. The smooth surface was ideal for halftone and color printing. By 1875 highquality machine-coated papers were used to reproduce halftone illustrations through a new photoengraving process. Coatings also improve the gloss and opacity of papers.

Diverse specialty papers are made for continually broadening applications. These papers differ through chemical additives and coatings. For instance, polyethylene-coated paper remains flexible from -65 to 200°F and it also resists creasing; this makes it ideal for packaging applications (bags, boxes, and package liners), as well as for disposable diapers, bibs, and bed sheets. Papers with a high content of rag fibers are extremely durable and therefore are used for bank notes and security notes, filter paper, tracing paper, and extremely lightweight special papers for printing Bibles and rolling cigarettes.

Growing more sophisticated as our communication needs have changed, the production of paper and writing materials has literally spanned the history of human civilization, going from cave paintings and indentations marked in clay tablets to processed plant materials such as bark cloth and papyrus, on to actual paper made from cellulose fibers, and to extremely durable polymer materials. But, with revolutionary advances in information storage technology, magnetic recording media and optical media, the next advance may be to eliminate paper entirely.

KEVIN J. ANDERSON

Advertisers in this issue	
AET addax	7
Gem Dugout	9
High Voltage Engineering Europa B.V.	inside front cover
Huntington Laboratories	9
Janis Research	10
LakeShore Cryotronics	5
Leybold Vacuum Products	11
Perkin Elmer	12
Quantum Design	inside back cover
Royal Society of Chemistry	22
UHV Instruments	back cover
Virginia Semiconductor	11
Voltaix	15

Polaroid International Instant Photomicrography Competition 1991

Polaroid Corporation announces its 10th annual competition designed to recognize the skills of light and electron micrographers who produce images on Polaroid instant films.

Cash awards will be made in each of five categories:

Electron: Life Science for electron micrographs of life science subjects on any Polaroid instant film.

Electron: Materials Science for electron micrographs of materials science subjects on any Polaroid instant film.

Optional Black-and-White for optical micrographs on any Polaroid instant black-and-white film.

Color for micrographs on any Polaroid instant color print or PolaChrome 35mm slide film.

Student micrographs on any polaroid instant film.

For details, contact: Polaroid International Instant Photomicrography Competition, Polaroid Corporation, 575 Technology Square-9P, Cambridge, MA 02139; phone (800) 225-1618.

Entries must be postmarked by August 31, 1991.