The origins of the kraft process

by A. J. Waugh*

The earliest human records were scratched, chiselled or chalked on cavern walls or stones. To obtain a more portable and convenient surface, the inventive Egyptians prepared a writing material from papyrus, a tall reed growing along the Nile, by criss-crossing peeled layers of the plant stem to form a sheet, using the reed sap as an adhesive. After drying in the sun, the papyrus sheet was rubbed with stone to produce a smooth surface that could be written on with ink. This form of paper is known to have been manufactured in Egypt as early as 2400 B.C., and many of the original manuscripts are still in existence.

A shortage of papyrus in Asia Minor led to the invention of parchment, which was made from dried calf or goat skin, treated for writing by rubbing chalk into the surface. A similar shortage of papyrus in Rome resulted in the use of wax covered boards, which were written on using a stylus. The early Greeks wrote their rent records and past due notices on broken pieces of pottery. The Chaldeans and Syrians wrote on soft clay bricks, which were then baked. It is probably no coincidence that the Chaldean librarians were the first to be conscripted whenever war appeared imminent.

The first people to make paper from pulp were probably the Chinese. The exact date of their discovery that fibres could be used in the papermaking process is not known, but most historians record it as about AD 105. It was that year that the invention was officially reported to the Emperor by Ts'ai Lun, to whom credit for the discovery is usually given.

The Chinese placed pieces of bamboo, rag and other fibrous material in pits of mud and water, and soaked them for about two weeks. The fibres were then separated by energetic pounding with a pestle. The process of recombining the fibres into a sheet was essentially the same as that used today in the manufacture of hand-made papers. Thus, by the time the Christian era was established in Europe, the art of papermaking was being widely practiced in China.

The Search for New Fibre Sources

Fibres from the inner bark of the mulberry tree were a major source of raw material in China. When the Arabs learned the craft of papermaking from Chinese prisoners in Samarkand about AD 750, they were forced to substitute linen rags, since mulberry trees were not readily available. The rags were disintegrated by boiling in an aqueous extract of wood ash. The alkaline residues of the wood ash were then washed out with water.

The secrets of the papermaking process gradually spread westward, and were carried into Europe as a

result of the invasions by various barbaric tribes. The Moors in Spain manufactured Europe's first paper, establishing a mill at Toledo as early as 1085 and another at Valencia at a later date. Paper was manufactured in Italy and France as early as 1200, and the first paper mill in Germany was erected in 1336. By the end of the 14th century, the process was firmly established throughout southern Europe, and gradually spread northward. The development of papermaking in England was comparatively slow, and it was not until three centuries later that the industry took firm hold there

During the middle ages the art of papermaking was slowly developed and improved. Alkaline solutions containing carbonates, lime or sodium hydroxide began to be used for pulping rags. The alkaline treatment was designed to remove fatty contaminants and coloring matter from linen or cotton rags, which were obtained from many sources, including the linen wraps from Egyptian mummies.

In the rag pulping process, some cellulose degradation and fibre modification necessarily took place, but rags required no delignification to separate the fibres. The discovery that hot aqueous alkali was capable of degrading and dissolving lignin in straw and other plant materials, to produce useful papermaking fibres, was not made in England until the 19th century.

During this era British industry and commerce reached a rate of development which has been surpassed only by that achieved in 20th century America. Paper was vitally necessary for the communication of information and ideas during this enormous commercial expansion. The stimulus for the successful researches into alkaline pulping was provided by the grave shortage of rags which resulted from the tremendous increase in the need for paper during the industrial revolution.

In 1800, Matthias Koops produced a pulp from straw, which contains about 16% lignin, by boiling it in a dilute



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alkali solution. Fibres from another annual plant, esparto grass, were shown to produce a finer paper than the rather poor quality straw pulp, and a patent on the pulping of esparto was taken out in 1861. This fibre is still used in the manufacture of some fine papers.

Chemical Pulping of Wood

In Hertfordshire in 1804, the Fourdrinier brothers began operating the predecessor of the paper machine that now bears their name. The Fourdrinier machine could supply enough paper to satisfy the existing demand, provided it had an ample supply of fibrous raw material.

Hugh Burgess and Charles Watt, who have frequently been cited as the inventors of the soda process, took up the search for a sufficient, inexpensive supply of raw material. The earlier investigations by Koops had shown that wood, containing 20 to 30% lignin, was more difficult to delignify than straw, but in 1851 Burgess and Watt developed their soda process, and were able to produce a satisfactory pulp from wood. The first stage of one of their processes consisted of treating wood

Fig. 1 The Marshall Boiler for digesting wood by the soda process, which is described by the inventor as having changed the manufacture of chemical wood pulp from the most disagreeable, offensive and wasteful process known in the whole art of paper making, to a pleasant, safe and economical system (1).

shavings with a sodium hydroxide solution at a higher concentration than had previously been used, in vessels similar to that illustrated (Fig. 1). The dark pulp, bleached by the further action of chlorine or chlorine compounds such as hypochlorite, was suitable for making a printing paper which cost only £20 per ton, as opposed to £40 per ton if made from rags.

The method was patented in 1853, but when Burgess and Watt offered the process to the British government, the offer was refused. This was indeed a surprising development, since the need was such that the proprietors of *The Times* of London in 1854 offered a reward of £1000 for the invention or discovery of a cheap substitute for rags (Cover photograph). It is possible that the government's refusal was based on the fact that Burgess and Watt did not describe a detailed method for the recovery of the alkali, although they did offer some suggestions in this connection.

Burgess, greatly disappointed, came to America, where his process was patented on July 1, 1854. In 1865, he and Morris L. Keen patented a process that also included the incineration of the spent liquor and

-Some Providence capitalists have just established a manufactory at Manayunk, Pa., near Philadelphia, which, by certain chemical processes, converts forty cords per day of poplar, maple and pine wood, into the whitest and best pulp for printing paper. The Manayunk Wood Pulp Co. has a working area of ten acres, \$450,000 invested in buildings, and a third as much in stock. The process of making paper pulp from wood was patented in England in 1853, and Mr. Burgess, the inventor, is now interested solely in this Manayunk mill. The wood is chopped up fine, and put into boilers, of which there are ten, holding two cords a piece. In these boilers is a heated chemical preparation, by which the cellular formation of the wood is destroyed and the fibrine preserved. The action of heat and chemicals reduces the wood to a perfect pulp, and from the boilers it passes through strainers and bleachery, coming out white and ready for the paper maker. To supply the mills with water a reservoir has been made, holding 5,500,000 gallons. Thirty thousand pounds of pulp are made every day. One hundred and fifty hands find employment here.

Fig. 2 Reproduction of a Boston newspaper clipping (ca. 1866) describing the Manayunk, Pa. soda mill, and the Burgess process.

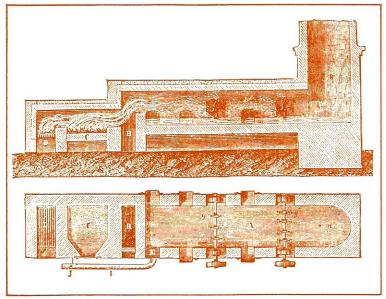


Fig. 3 An illustration of the Porrion oven for sodium recovery. Davis (1) writes that "the economical regeneration of the carbonate of sodium... of the black liquors produced by the soda treatment of straw, wood, etc., have been a progress of the highest importance in these industries."

which enabled most of the alkali used in the process to be recovered. Burgess' interest in the process led to the building of a soda pulp mill at Manayunk, Pa. which was completed in April, 1866 (Fig. 2). The soda process, except for some new developments and modifications in equipment, has remained essentially unchanged to this day (Fig. 3).

The Kraft Process

In the kraft process a mixture of sodium hydroxide and sodium sulphide is used to pulp the wood. The sulphide accelerates delignification, which means that the chips are exposed to the hot alkali for a shorter time than in the soda process. This makes it possible to produce a pulp that is much stronger than soda pulp.

The first patents on the use of sulphides in wood pulping are those of Eaton in the United States in 1870 and 1871 (Fig. 4), and there is some evidence that experiments with sulphides were carried out in England during the Napoleonic Wars (i.e., 1805-1814). In spite of this, C. F. Dahl of Danzig, Germany, is usually credited with the development of the kraft, or sulphate process. Dahl's original intention was to reduce manufacturing costs, by substituting sodium sulphate (salt cake) for the more expensive sodium carbonate (soda ash), used to replace chemicals which were lost during soda pulping. After several years of studies, Dahl obtained a patent for his process in 1884.

In the chemical recovery process, sodium sulphate is reduced to sodium sulphide in the recovery furnace. Although sodium sulphate itself is incapable of delignifying wood, the use of this salt to replace chemical losses has given rise to the term "sulphate pulping" to describe this process.

The sulphate process was soon applied to the pulping of coniferous woods, and was well received in the

ASAHEL K. EATON, OF PIERMONT, NEW YORK. Letters Patent No. 100,143, dated August 9, 1870. IMPROVEMENT IN THE MANUFACTURE OF PAPER PULP. The Schedule referred to in these Letters Patent and making part of the same.

Fig. 4 Reproduction of the 1870 Patent, issued to A. K. Eaton, which describes the use of sulphide "as a solvent in the manufacture of paper pulp from straw, wood or other vegetable substance suitable for that purpose."

Scandinavian countries, where it was utilized to produce pulp from vast quantities of sawmill refuse and smaller sizes of wood, which had previously either been used as cheap fuel or wasted.

The first kraft pulp was produced at the Munksjö mill in Jönkoping, Sweden in 1885. Apparently, a digester was inadvertently blown before the sulphate cooking process was complete, but instead of discarding the chips, the mill manager ordered them to be passed through a kollergang (a type of refiner) to salvage an inferior grade of pulp from the mistake. The result was a dark colored paper which was far stronger than any paper previously known. The new paper was given the name kraft, which is Swedish and German for strength, and the more distinctive term "kraft pulp" usually refers to the strongest unbleached sulphate pulps.

Following this development many soda mills were converted to the kraft process, in order to compete with mills using the acid sulphite process, which was developed commercially between 1874 and 1881. Although sulphite pulp was stronger, cheaper and lighter in color than soda pulp, the advent of the kraft process reduced production costs and gave a product which was stronger, though considerably darker, than sulphite pulp.

The first kraft pulp in North America was produced at the Brompton Pulp and Paper Company, East Angus, Quebec, in 1907. In the United States, the product was first introduced in the south, and by 1911, the Letcher-Moore Lumber Co. of Orange, Texas was successfully turning out a sound, commercial kraft product.

Reference

(1) Charles Thomas Davis, The Manufacture of Paper, published by Henry Carey Baird & Co., Philadelphia, 1886.