6 Paper and Paper-Based Packaging Materials

6.1 PULP

Pulp is the fibrous raw material for the production of paper, paperboard, corrugated board and similar manufactured products. It is obtained from plant fiber and is therefore a renewable resource. Paper derives its name from the reedy plant papyrus, which the ancient Egyptians used to produce the world's first writing material by beating and pressing together thin layers of the plant stem. However, complete defibering which is characteristic of true papermaking was absent (Smook, 2002). The first authentic papermaking, which is the formation of a cohesive sheet from the rebonding of separated fibers, has been attributed to Ts'ai-Lun of China in 105 AD, who used bamboo, mulberry bark and rags.

Since then, many fibers have been used for the manufacture of paper including those from flax, bamboo and other grasses, various leaves, cottonseed hair and the woody fibers of trees. The influence of the raw material can be largely assigned to the length and wall thickness of the fibers rather than to their chemical composition. About 97% of the world's paper and board is made from wood pulp and about 85% of the wood pulp used is from spruces, firs and pines—coniferous trees that predominate in the forests of the north temperate zone. Today, an increasing quantity of wood pulp is being sourced from sustainably managed forests, defined as "the stewardship and use of forests and forest lands in a way, and at a rate, that maintains their biodiversity, productivity, regeneration capacity, vitality and their potential to fulfill, now and in the future, relevant ecological, economic and social functions, at local, national and global levels, and that does not cause damage to other ecosystems." Although there are more than 50 certification standards worldwide for sustainably managed forests, the two largest umbrella certification programs are those of the Programme for the Endorsement of Forest Certification (PEFC) schemes and the Forest Stewardship Council (FSC).

There are three main constituents of the wood cell wall:

1. *Cellulose.* This is a long-chain, linear polymer built up from a large number of glucose molecules (weight-average DP 3500 for native wood cellulose in situ) and is the most abundant, naturally occurring organic compound. The fiber-forming properties of cellulose depend on the fact that it consists of long, relatively straight chains that tend to lie parallel to one another. Cellulose is moderately resistant to the action of chlorine and dilute sodium hydroxide under mild conditions, but is modified or dissolved under more severe conditions. It is relatively resistant to oxidation (e.g., with bleaching agents), and, therefore, bleaching operations can be used to remove small amounts of impurities such as lignin without appreciable damage to the strength of the pulp.

2. *Hemicelluloses.* These are lower MW (weight-average DP 15) mixed-sugar polysaccharides consisting of one or more of the following molecules: xylose, mannose, arabinose, galactose and uronic acids, with the composition differing from species to species. The principal hemicelluloses are xylan in hardwoods and glucomannon in softwoods. Hemicelluloses are usually soluble in dilute alkalis. The quantity rather than the chemical nature of the hemicelluloses appears to determine the paper properties. Hemicelluloses are largely responsible for hydration and development of bonding during beating of chemical pulps.

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3. *Lignin*. This is the natural binding constituent of the cells of wood and plant stalks. It is a highly branched, three-dimensional (3D), alkylaromatic, thermoplastic polymer of uncertain size, built up largely from substituted phenylpropane or propylbenzene units. Hydroxyl or methoxyl groups are attached to the benzene carbon atoms. It has no fiber-forming properties and is attacked by chlorine and sodium hydroxide with formation of soluble, dark brown derivatives. It softens at about 160°C.

6.1.1 INTRODUCTION TO PULPING

The cell walls of softwoods, which are preferred for most pulp products, typically contain 40%–44% cellulose, 25%–29% hemicelluloses and 25%–31% lignin by weight (Smook, 2002). The average composition of softwoods and hardwoods is shown in Figure 6.1. Compared to hardwoods, softwoods have fibers that are generally up to 2.5 times longer. As a result, hardwoods produce a finer, smoother but less strong sheet.

Pulping refers to the process wherein wood or other fibrous raw materials are reduced to a fibrous mass. The purpose of pulping is to separate the fibers without damaging them so that they can then be reformed into a paper sheet in the papermaking process. The intercellular substances (primarily lignin) must be softened or dissolved to free individual fibers. Commercial pulping methods take advantage of the differences between the properties of cellulose and lignin in order to separate fibers. However, breaking and weakening of the fibers does occur to a greater or lesser degree at various stages during the pulping process.

Pulping is accomplished by either mechanical, thermal, chemical or a combination of these treatments. Pulps that retain most of the wood lignin consist of stiff fibers that do not produce strong papers; they deteriorate in color and strength quite rapidly. These properties can be improved by removing most or all of the lignin by cooking wood with solutions of various chemicals; the pulps thus produced are known as *chemical pulps*. In contrast, *mechanical pulps* are produced by pressing logs onto a grindstone when the heat generated by friction softens the lignin so that the fibers separate with very little damage. Mechanical pulps can also be formed by grinding wood chips

Softwoods		Hardwoods
	Cellulose Long chains, unbranched molecules	
42% ± 2%		45% ± 2%
	Hemicelluloses Branched, short chain molecules	
27% ± 2%		30% ± 5%
	Lignin Three dimensional phenolic polymer network	
28% ± 3%		20% ± 4%
3% ± 2%	Extractives	5% ± 3%

FIGURE 6.1 Average composition of softwoods and hardwoods. (Adapted from Smook, G.A., *Handbook for Pulp and Paper Technologists*, 3rd edn., Angus Wilde Publications, Canada, Vancouver, 2002.)

between two rotating refiner plates. In addition, there are some processes which are categorized as *semichemical* and *chemimechanical*. The most prevalent process is chemical pulping, which accounts for >70% of the worldwide production of pulp, of which kraft pulping is the most prevalent at 80% (Kadla and Dai, 2006).

6.1.2 Mechanical Pulps

Groundwood pulp is produced by forcing wood against a rapidly revolving grindstone. Practically all the wood fiber (both cellulose and lignin) is utilized. This contrasts with several chemical processes where the lignin is dissolved to varying degrees. As a result, the yield of chemical pulp is about one-half that of the mechanical process. The fibers vary in length and composition since they are effectively torn from the pulpwood.

Groundwood pulp contains a considerable proportion (70%–80%) of fiber bundles, broken fibers and fines in addition to the individual fibers. The fibers are essentially wood with the original cell-wall lignin intact. Therefore, they are very stiff and bulky, and do not collapse like the chemical pulp fibers. Although mechanical pulps have a high energy demand, they are relatively low in cost because of the high yield (Kadla and Dai, 2006).

Most groundwood pulp is used in the manufacture of newsprint and magazine papers because of its low cost and quick ink-absorbing properties (a consequence of the frayed and broken fibers). It is also used as board for folding and molded cartons, tissues and similar products. The paper has high bulk and excellent opacity, but relatively low mechanical strength.

Mechanical pulps can be bleached using oxidative (e.g., hydrogen peroxide and sodium hypochlorite) or reductive (e.g., sodium hydrosulfite) bleaching agents. Bleaching is done in a lignin-conserving manner called *brightening* in which the chromophores are modified and little solubilization of the lignin occurs. Paper and paperboard containing mechanical pulps have poor brightness stability, even after bleaching, particularly in the presence of UV radiation.

In the 1950s, the *refiner mechanical pulping* (RMP) process was developed, which produced a stronger pulp and utilized various supplies of wood chips, sawmill residues and sawdust. RMP results in more long fibers than stone groundwood and subsequently stronger paper. However, the energy requirements of RMP are higher and the pulp does not have the opacity of groundwood fibers (Kadla and Dai, 2006).

Thermomechanical pulping (TMP) presteams chips between 110°C and 150°C so that they become malleable and do not fracture readily under the impact of the refiner bars. This material is highly flexible and gives good bonding and surface smoothing to the paper. The production of TMP pulps increased dramatically after its introduction in the early 1970s because they could be substituted for conventional groundwood pulps in newsprint blends to give a stronger paper.

Chemithermomechanical pulping (CTMP) increases the strength properties of TMP pulps even further by a mild pretreatment with sodium sulfite. CTMP pulps are obtained by a comparatively mild chemical treatment followed by pressurized refining. In general, CTMP pulps have a greater long fiber fraction and lower fines fraction than comparable TMP pulps. CTMP is suitable for the middle layer of multi-ply boards where it adds bulk and rigidity (stiffness) at lower cost than kraft pulp.

6.1.3 Chemical Pulps

There are several chemical pulping methods, each of which are based, either directly or indirectly, on the use of sodium hydroxide. The primary goal of chemical pulping is to selectively remove as much lignin as possible, especially from the middle lamella, without degrading the carbohydrate components and negatively effecting pulp properties. Therefore, the nature of the pulping chemicals influences the properties of the residual lignin and the residual carbohydrates, and the selectivity

of delignification is determined by the weight ratio of lignin removal to carbohydrate removal. The pulp and paper industry uses the "kappa number" to express the lignin content of a pulp, a high kappa number indicating a high lignin content. The kappa number of bleachable softwood and hardwood pulps is 30–40 and 18–20, respectively (Kadla and Dai, 2006). For the production of chemical pulps, the bark is removed and the logs are passed through a chipper. The chipped wood is charged into a digester with the cooking chemicals, and the digestion carried out under pressure at the required temperature.

6.1.3.1 Alkaline Processes

6.1.3.1.1 Soda Process

The first process for the manufacture of chemical wood pulp was invented by Englishmen Hugh Burgess and Charles Watt in 1851 and was patented in 1854. The first successful soda mill commenced operation in 1866. The soda process consisted of boiling wood in 4%–6% sodium hydroxide liquor at a high temperature (170°C). A later patent in 1865 covered the incineration of the spent soda liquor to recover most of the alkali used in the process (Smook, 2002). Less than 2% of the pulp produced today uses this process which is very similar to the sulfate process, except that only sodium hydroxide is used. Essentially all former soda mills have converted to the sulfate process.

6.1.3.1.2 Sulfate (Kraft) Process

In 1879, German chemist Carl F. Dahl developed the sulfate method of pulping wood. The process was essentially a modification of the soda process, but instead of sodium hydroxide, sodium sulfate was the major chemical used as the cooking liquor. The new sulfate process produced a much stronger pulp which is more commonly known as *kraft* pulp after the German and Swedish word for strength. Although Dahl commenced construction of a kraft mill in his native Germany, it was never completed due to lack of finance (Ainsworth, 1959). He moved to Sweden and the first kraft mill was built in Munksjö, Sweden in 1885. The location of the first kraft mill in the United States is disputed; one author (Smook, 2002) claims it was built in 1911 in Pensacola, Florida, while another (Ainsworth, 1959) states that the Halifax Paper Company in Roanoke Rapids, North Carolina made the first kraft pulp.

Today, the sulfate process is the dominant chemical wood pulping process and uses an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide known as "white liquor" for cooking the chips. It takes its name from the fact that sodium sulfate (or bisulfate) was used as the make-up chemical in the recovery process, with sodium sulfate being reduced to sodium sulfide in the recovery furnace by reaction with carbon. The sulfate process has the ability to pulp any wood species, particularly pines, which are more resinous than firs and spruces and not easily pulped by the acid sulfite process.

Pulp produced by this process is stronger than that produced from the same wood by the acid sulfite process, and the use of sulfate pulps in liner board has enabled the replacement of wooden cases by corrugated cartons. The sulfate and acid sulfite processes together account for over 90% of the chemical wood pulp currently produced in the world.

6.1.3.2 Sulfite Processes

The invention of this process is generally credited to the American chemist Benjamin Chew Tilghman who, in 1857, found that wood could be softened and defibered with a solution of calcium bisulfite ($Ca(HSO_3)_2$) and sulfurous acid. Swedish chemist Carl Daniel Ekman treated wood with magnesium bisulfite in 1870 and constructed the first sulfite paper mill in 1872 in Bergvik, Sweden. A German modification of the American sulfite process was developed by the German chemist Dr Alexander Mitscherlich and involved cooking (using indirect steam heating) at lower

temperatures and pressures and for longer times than previously. This was the dominant pulping process until 1937 when kraft pulping became the foremost chemical pulping process.

Several pulping processes are based on the use of sulfur dioxide as the essential component of the pulping liquor. Sulfur dioxide dissolves in water to form sulfurous acid, and a part of the acid is neutralized by a base during preparation of the pulping liquor. The various sulfite processes differ in the kind of base used and in the amount of base added. These differences govern the resulting acidity or pH of the liquor. These processes depend on the ability of sulfite solutions to render lignin partially soluble.

For certain applications, sulfite pulps are still preferred and remain an important commodity, especially for specialty papers (e.g., glassine) and as a source of cellulose for non-paper applications. Sulfite pulps have higher brightness, higher yields at a given kappa, lower odor and lower investment costs as compared to kraft pulps (Kadla and Dai, 2006). A special grade of bleached sulfite pulp is known as "dissolving pulp" and is used for a variety of cellulose derivatives including RCF and cellulose acetate.

6.1.4 SEMICHEMICAL PULPS

Semichemical pulping combines chemical and mechanical methods in which wood chips are partially softened or digested with conventional chemicals, such as sodium hydroxide, sodium carbonate or sodium sulfate, after which the remainder of the pulping action is supplied mechanically, most often in disk refiners.

The object of this process is to produce as high a yield as possible commensurate with the best possible strength and cleanliness. The hemicelluloses, mostly lost in conventional chemical digestion processes, are retained to a greater degree and result in an improvement in potential strength development. Although less flexible, semichemical pulps resemble chemical pulps more than mechanical pulps.

The *neutral-sulfite semichemical* (NSSC) process (applied mainly to hardwood chips) uses sodium sulfite and a small amount of sodium hydroxide or sodium carbonate to give a slightly alkaline liquor. The NSSC pulp is obtained in higher yield but with higher lignin content than in the other sulfite processes. It is used mainly for the manufacture of corrugating medium.

6.1.5 DIGESTION

The digestion process essentially consists of treating wood in chip form in a pressurized vessel under controlled conditions of time, liquor concentration and pressure/temperature. The main objectives of digestion are as follows:

1. To produce a well-cooked pulp, free from the noncellulosic portions of the wood (i.e., ligninand to a certain extent hemicelluloses)
2. To achieve a maximum yield of raw material (i.e., pulp from wood) commensurate with pulp quality
3. To ensure a constant supply of pulp of the correct quality

Currently, most pulping processes are continuous, and to give an indication of the processing conditions encountered, the widely used Kamyr continuous digester is now briefly described. After steaming at low pressure, during which time turpentine and gases are vented to the condenser, the chips are brought to the digester pressure of 1000 kPa. They are picked up in a stream of pulping solution and their temperature is raised to 170°C over 1.5 h. After holding at this temperature for a further 1.5 h, the digestion process is essentially complete.

After digestion, the liquor containing the soluble residue from the cook is washed out of the pulp, which is then screened to remove knots and fiber bundles that have not fully disintegrated. The pulp is then sent to the bleach plant or paper mill.

6.1.6 BLEACHING

Bleaching is a chemical process applied to chemical and mechanical pulps, primarily to increase their brightness but it also improves the cleanliness of pulp through removing extractives and other contaminants. Pulps vary considerably in their color after pulping, depending on the wood species, method of processing and extraneous components. The whiteness of pulp is measured by its ability to reflect monochromatic light in comparison to a known standard (usually magnesium oxide). Brightness is an index of whiteness, measured as the reflectivity of a paper sample using light at 457 nm. Unbleached pulps exhibit a range of brightness values from 15 to 60. Cellulose and hemicellulose are inherently white and do not contribute to color; it is the chromophoric groups on the lignin that are largely responsible for the color of the pulp.

Basically, there are two types of bleaching operations: Those that chemically modify the chromophoric groups by oxidation or reduction but remove very little lignin or other substances from the fibers, and those that complete the delignification process and remove some carbohydrate material. To fully remove lignin from pulp, multiple bleaching stages are required. In a typical bleaching process, individual bleaching stages are generally separated by washing stages to remove residual chemicals and degraded lignin.

Chemical methods must be used to improve the color and appearance of the pulp; these are bleaching treatments and involve both the oxidation of colored bodies and the removal of residual encrusting materials (the principal one being lignin) remaining from the digestion and washing stages. Since bleaching reduces the strength of the pulp, it is necessary to reach a compromise between the brightness of the finished sheet and its tensile properties.

In 1986, the production process for bleached chemical pulp was identified as a major contributor of polychlorinated dioxins and dibenzofurans to the environment. Because these compounds are powerful toxins and carcinogens (see Section 22.5.1 for further discussion), considerable investigative activity was carried out in Europe and North America to identify point sources and corrective measures (Smook, 2002). Chlorine bleaching was identified as the major source of these compounds. In addition to dioxins and furans, a host of other chlorinated organic compounds (known collectively as *adsorbable organic halides* or AOX) are formed during chlorine bleaching. Strict regulations now limit the production of these chlorinated compounds, resulting in a move away from molecular chlorine bleaching to chlorine dioxide (so-called ECF or elemental chlorine free bleaching) and to oxygen and peroxide (so-called TCF or total chlorine free bleaching). These changes have been introduced to enable pulp and paper mills to meet tough new antipollution laws and regulations, and to conserve wood, chemicals and energy (Bajpai, 2010).

6.1.6.1 Mechanical Pulps

Lignin is the main contributor to the color of mechanical pulps. An increase in the brightness of mechanical pulps is achieved by modifying the lignin structures (chromophores) in the pulp furnish. The process is sometimes referred to as brightening to distinguish it from lignin-removing bleaching methods for chemical pulps (Ni and Liu, 2002).The most effective bleaching agent for most groundwoods is hydrogen peroxide, and since the bleaching is performed in alkaline solutions, sodium peroxide is also used. The reaction typically requires 3 h at 40°C and is followed by neutralization and destruction of excess peroxide with SO_2.These pulps may be improved in color to only a limited extent since they contain virtually all the lignin from the original wood. Peroxide bleaching allows brightness to be increased by nearly 20%.

6.1.6.2 Chemical Pulps

The residual lignin content in chemical pulp accounts for 2%–5% of the mass and is responsible for the dark color of the unbleached pulp. The reagents for full bleaching of chemical pulp are mostly oxidative and since the carbohydrates are also susceptible to oxidation, bleaching must be accomplished under the mildest conditions. Bleaching of chemical pulps is basically stepwise purification

of colloidal cellulose, and bleaching can therefore be regarded as a continuation of the cooking process. The bleaching of pulp is done through chemical reactions of bleaching agents with lignin and coloring matter in the pulp. The bleaching is performed in a number of stages utilizing one or more of the following: chlorine dioxide, oxygen, ozone and peroxide. Between these stages, the pulp is treated with alkali to dissolve degradation products. Full details of these processes are given elsewhere (Dence and Reeve, 1996; Ni and Liu, 2002).

6.1.6.3 Recycled Pulps

Recycled or secondary fibers are an important raw material in terms of volume and utilization for the paper industry in many countries, due to market pressures resulting from government legislation, increasing public awareness of issues like sustainability and a dwindling supply of virgin fibers in some regions. The recycling of paper is an example of the sustainable use of resources, and although recycling is generally both economically and ecologically sound, recovered paper cannot be used in all paper grades. The quality and brightness of the recycled fiber furnish will dictate its end use. The removal of colored complexes such as dyes and other unwanted materials (i.e., ink and stickies) is an important operation to produce a recycled pulp with good properties. Generally, the conditions used for bleaching/brightening of recycled fibers are similar to those used for mechanical and chemical pulps.

6.2 PAPER

Stock preparation is the interface between the pulp mill and the papermaking process in which pulp is treated mechanically and, in some instances, chemically by the use of additives and is thus made ready for forming into a sheet or board on the paper machine. During the stock preparation steps, the pulps are most conveniently handled as aqueous slurries. However, in the papermaking process utilizing purchased pulps and waste paper which are received as dry sheets, the first step is the separation of all the fibers from one another, and their dispersion in water with a minimum of mechanical work to avoid altering the fiber properties. This process is known as slushing or repulping and is carried out in a machine such as the hydrapulper (see Figure 6.2), so-called because of the hydraulic forces that are developed. When the pulping and papermaking operations are adjacent to one another, pulps are usually delivered to the paper mill in slush form directly from the pulping operation.
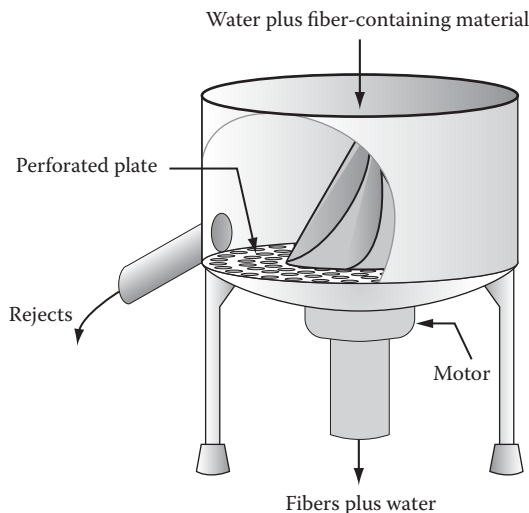
FIGURE 6.2 Batch hydrapulper.

6.2.1 Beating and Refining

Stock—as fibrous material is commonly called—is prepared by two chief processes commonly referred to as *beating* and *refining*. Both operations are fundamentally the same; in many situations, the two terms are used synonymously. Beating and refining are used to improve the strength and other physical properties of the finished sheet, and to influence the behavior of the system during the sheet-forming and drying steps (Hubbe, 2005).

The object of beating is to increase the surface area of the fibers by assisting them to imbibe water. As a result, additional bonding opportunities are provided for between cellulose molecules of neighboring fibers. The beating also makes the fibers more flexible, causing them to become relatively mobile and to deform plastically on the paper machine. The mixture of pulp (known as the *furnish*) is passed into the beater and brought to a consistency of 5%–7%. The fibers are then beaten while suspended in the water in order to impart to them many of the properties that will determine the character of the final product.

The quality and characteristics of the finished paper depend to a great extent on the treatment in the beater. Because papermaking fibers are stiff and springy, the resulting paper would be flabby and weak if made into a sheet of paper without beating. There would be little adhesion between the fibers and they could not be consolidated under the presses of the paper machine. A sheet formed from an unbeaten pulp has a low density, and is rather soft and weak, whereas if the same pulp is beaten, then the resultant paper is much more dense, hard and strong. If taken to the extreme, beating produces very dense, translucent, glassine-type sheets (Hubbe, 2005). Thus, beating can be controlled to produce paper types as widely different as blotting and greaseproof paper.

Since its invention in Holland around 1690, the principle of the batch-operated hollander beater has remained substantially the same. It consists of a cylindrical roll containing rectangular, blunt-tipped blades (bars) that revolves over a stationary bedplate which also contains a set of bars. Circulating stock passes between the roll and the bedplate; the severity of beating is controlled by adjusting the load of one against the other. Circulation is continued until the pulp is considered ready to be made into the desired paper. In many paper mills, beaters have been replaced by continuous refiners, such as disk refiners (where rotary disks rotate against a working surface) and conical refiners. However, the batch beater is a convenient vessel for adding chemicals and mixing them intimately with the pulp in order to give special properties to the final paper.

In papermaking, chemicals such as strength additives, adhesives, mineral fillers and sizing agents may be added at the beater stage prior to sheet formation (i.e., internal addition), or to the resulting sheet after complete or partial drying, depending primarily on the desired effects. Strength additives are usually added internally if uniform strength throughout the sheet is desired, but they are applied to the surface if increased surface strength is needed. Fillers can improve brightness, opacity, softness, smoothness and ink receptivity, and are essentially insoluble in water under the conditions of use. Because filler particles are much smaller than the fibers used in papermaking, often ~0.5 to 3 mm in diameter, they usually contribute to a smoother product. Fillers also tend to increase the efficiency with which light is scattered by paper, yielding increases in the paper's opacity and brightness (Hubbe, 2005). Calcium carbonate is the most important papermaking filler followed by kaolin clay, with limited use of titanium dioxide. The main drawback is that the materials added may be lost through the wire of the paper machine in the large amount of water used. Therefore, if an additive cannot be retained efficiently from dilute pulp slurry, then it is better to apply it to the surface of the sheet (Dulany et al., 2011).

Sizing is the process of adding materials to the paper in order to render the sheet more resistant to penetration by liquids, particularly water. Rosin is the most widely used sizing agent, but starches, glues, caseins, synthetic resins and cellulose derivatives are also used (Dulany et al., 2011). The sizing agents may be added directly to the stock as beater additives to produce internal or engine sizing. Alternatively, the dry sheet may be passed through a size solution to produce a surface size (see Section 6.1.3.2).

The required wet strength (up to 50% of the dry paper strength can be retained) is obtained with the aid of wet-strength additives that are capable of covalently bonding in order to preserve paper strength in the presence of water. Linerboard, carrierboard, bleached carton and liquid paperboard are some of the principal grades that require an amount of wet strength to be functional. There are two theories regarding the mechanism of wet strength (Auhorn, 2006). The first states that the wet strength effect is due, at least in part, to a reaction between the resin and the cellulose, which leads to the formation of ether bonds. The second theory assumes that the wet strength additives cross-link on exposure to heat in the dryer section to form a 3D network, wrap themselves around the points where the fibers intersect and thus protect the points of intersection from water penetration and swelling.

The most widely used class of such additives is the polyamidoamine-epichlorohydrin (PAAE) resins which were first introduced in the late 1950s. During the formation of a PAAE resin, the epichlorohydrin can be hydrolyzed to produce 3-monochloropropane-1, 2-diol (3-MCPD) which is not an approved food additive or GRAS. Although 3-MCPD has not been proven carcinogenic to humans, there is sufficient human health concern that threshold levels have been established. Pace and Hartman (2010) detected 3-MCPD at up to 9.87 mg kg^{-1} (ppm) in polyethylene-coated bleached paperboard and showed that it does not migrate through the polyethylene food contact surface into an aqueous/acidic food simulant. They also demonstrated that no significant amount of 3-MCPD migrated from the unskived seam edges on the food contact side of the paperboard structure.

Braga et al. (2009) gave the history and current status of regulations in Germany with respect to chlorinated monomers like DCP (dichloropropanol) and MCPD from wet-strength additives. They are associated with AOX emissions in the effluent from paper mills. Today's products (3rd generation) offer DCP contents in the ppm range compared to values of up to 1% in 1st generation products. As a result, papermakers now have a choice of products meeting all environmental regulations.

6.2.2 Papermaking

6.2.2.1 Fourdrinier Machine

The principle of operation of the modern paper machine differs little from that of the first Fourdrinier machine of 1804, named after its financiers Henry and Sealy Fourdrinier, two prosperous London stationers who purchased the patent interests of the Frenchman Didot Frères. He had obtained the patent rights from a clerk (one Louis Robert) at his mill who had built a paper machine in 1799. On behalf of the Fourdrinier brothers, Englishman John Gamble commissioned the engineering firm of Hall to build a prototype. The task was assigned to one of Hall's apprentices, Bryan Donkin (who was also involved in the development of the tinplate can [see Chapter 7]). The Fourdrinier brothers spent the whole of their private fortune in developing a practical paper machine, eventually becoming bankrupt and dying in poverty. Despite their misfortune, their name has been familiar to generations of papermakers for the development of a machine, the essential principles of which are still in use today.

Paper is made by depositing a very dilute suspension of fibers from a very low consistency aqueous suspension (greater than 99% water) on to a relatively fine woven screen, over 95% of the water being removed by drainage through the wire. The fibers interlace in a generally random manner as they are deposited on the wire and become part of the filter medium.

Although paper is the general term for a wide range of matted or felted webs of vegetable fiber that have been formed on a screen from a water suspension, it is usually subdivided into paper and paperboard. However, there is no rigid line of demarcation between the two, with structures <300 μm thick being considered paper regardless of the grammage or weight per unit area. Paper is generally termed paperboard when its basis weight (grammage) exceeds 250 g m^{-2} (i.e., grams per square meter or gsm), but there are exceptions (see Section 6.3).
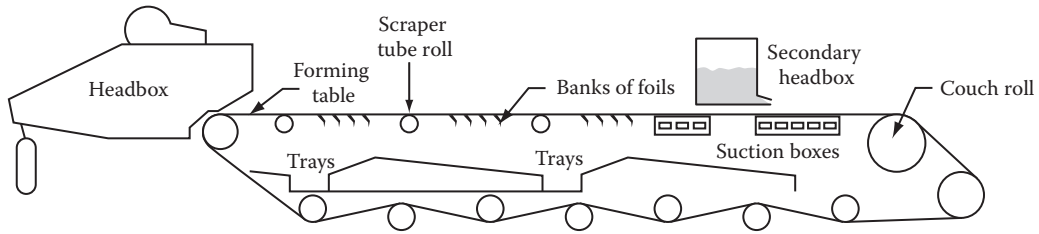
FIGURE 6.3 Fourdrinier machine. (Redrawn from Paper, in: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam, K.L. (Ed.), John Wiley & Sons, New York, pp. 908–912, 2009. Reproduced with permission.)

The modern Fourdrinier paper machine consists essentially of an endless woven wire gauze or forming fabric stretched over rollers. The forming section of a Fourdrinier machine (illustrated in Figure 6.3) is made up of two essential parts: the flow box and the drainage table. The operation of both parts can influence the structure of the resulting paperboard web (Attwood, 2009). The concentration of the fiber suspension delivered to the moving screen is generally 0.4%–1.2% and increases as a result of free drainage through the screen. The relative speeds of the stock and wire affect the degree to which the fibers are aligned along the direction of travel. The concentration increases between 3% and 4% further down the Fourdrinier table where a vacuum is applied in the suction boxes. For the production of multi-ply paperboard, a secondary flow box is often used. Fourdrinier machines are standard in the industry and are used to produce all grades of paper and paperboard.

6.2.2.2 Cylinder Machine

A second system was developed in 1809 by John Dickinson of England and is known as the cylinder or vat machine process. A cylinder covered with a wire cloth is rotated partially submerged in a stock suspension. Because of a vacuum applied inside the cylinder, water drains inward through the wire cloth, and the paper web is formed on the outside. The web is picked up by a felt, which is pressed onto the top of the cylinder by a rubber roll. A series of vats provide individual plies of fiber which are subsequently matted together. Cylinder machines are used to produce heavy multi-ply boards. They produce a sheet that is much stronger in the direction of flow than that produced on Fourdrinier machines.

Cylinder-vat formation differs basically from Fourdrinier formation because the cylinder picks up individual fibers from the stock suspension, in contrast to the Fourdrinier wire on which fibers are deposited from an inflowing stock suspension where water is immediately removed by draining.

The advantage of the cylinder machine for the manufacture of boards is that a number of cylinder units can be arranged so that the fiber mat from each is deposited as a layer and all the layers can be combined to make a multi-ply paperboard.

6.2.2.3 Twin-Wire Formers

The twin-wire method for forming paper and paperboard was developed in the United Kingdom in the 1950s. The paper web is formed between two converging forming screens by means of a flow box and the water is drained from the slurry by pressure and later by vacuum. A typical twin-wire forming unit is the Inverform (shown in Figure 6.4), which was designed to provide a new method for the manufacture of single and multi-ply sheets at high speeds. Successive layers of fiber are laid down sequentially on the felt, with water being removed upwardly, overcoming the difficulty experienced in the conventional downward removal of water through several layers of board at high speed.

Twin-wire formers have replaced the Fourdrinier wet ends on many machines, particularly for lightweight sheets, corrugated media and linerboard grades.
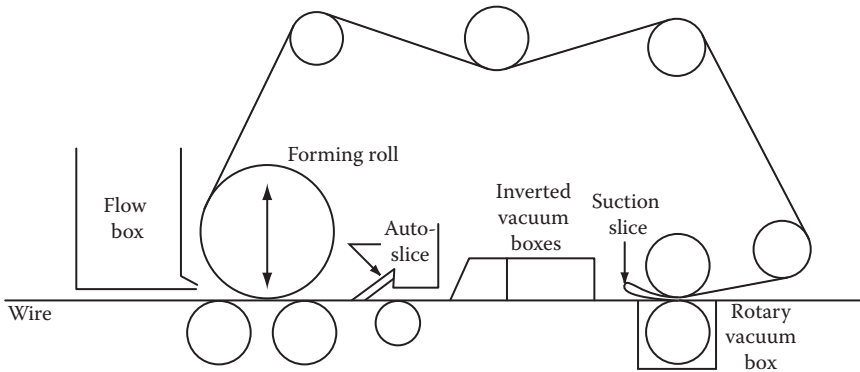
FIGURE 6.4 Inverform twin-wire forming unit. (Redrawn from Paper, in: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam, K.L. (Ed.), John Wiley & Sons, New York, pp. 908–912, 2009. Reproduced with permission.)

6.2.2.4 Presses and Dryers

After leaving the forming fabric of the papermaking machine, the sheet (which has a moisture content of 75%–90% depending on type) passes to the press and dryer sections for further water removal. Rotary presses (which may have solid or perforated rollers, often with internal suction) receive the sheets on continuous felts, which act as conveyers and porous receptors of water. On leaving the press, the moisture content is typically 60%–70%, again depending on type.

The paper is then passed through a series of steam-heated rollers and dried to a final moisture content between 4% and 10%. Other types of dryers are used for special products or situations. For example, the Yankee dryer is a large, steam-heated cylinder, which dries the sheet from one side only, and is used extensively for tissues and to produce *machine glazed* (MG) papers, the latter having a glazed or shiny surface from intimate contact with the polished dryer surface.

6.2.3 CONVERTING

Almost all paper is converted by undergoing further treatment after manufacture, such as embossing, impregnating, saturating, laminating and the forming of special shapes and sizes such as bags and boxes. Further surface treatment involving the application of adhesives, functional products and pigments are common, depending on the end use of the paper. The incorporation of strength additives, adhesives, fillers and sizing agents throughout the whole paper was briefly described in Section 6.2.1. Surface treatment applies similar materials on the web.

Because of the widespread use of paper and paperboard in direct contact with foods, most mills use paper chemicals that have been cleared for use with food by regulatory authorities such as the U.S. Food and Drug Administration (FDA).

6.2.3.1 Calendering

In many applications, the surface of the sheet needs improvement so that any characters imposed on the sheet are legible. This is achieved by calendering, a process that reorients the surface fibers in the base sheet of paper (or the coating applied to the surface) through the use of pressure. This serves to smooth the surface, control surface texture and develop a glossy finish. Such papers are known as *machine finished* (MF).

Supercalendering, as well as smoothing the surface of the sheet by pressure, also alters the optical reflectance of the sheet by friction, giving a higher finish than that obtained on calenders. As the paper passes between steel or fiber rollers under great pressure, moisture is added. Only the bottom roller is powered; the others provide a certain amount of slippage which irons the sheet.

The slipping action of the sheet against the polished steel rollers results in a gloss while smoothing and leveling the surface contours.

6.2.3.2   Sizing

Surface treatments such as sizing and coating are extensively applied to improve the appearance of products. Paper may be coated either on equipment that is an integral part of the paper machine (i.e., on-machine coating) or on separate converting equipment. The most common method for the application of chemicals to the surface of a paper web is with a size press, where dry paper is passed through a flooded nip and a solution or dispersion of the functional chemical contacts both sides of the paper. Excess liquid is then squeezed out in the press and the paper is redried (Dulany et al., 2011).

Surface-sizing agents prevent excess water penetration and improve the strength of the paper. The sizing agent penetrates far enough into the paper to increase the fiber bonding and the dependent properties such as bursting, tensile and folding strengths (Rhim, 2010). An additional effect is an improvement in the scuffing resistance of the paper surface.

The most commonly used materials for surface sizing are starches, usually chemically modified (e.g., oxidized starches, cationic starches and hydroxyethylated derivatives). They are used not only for sizing, but also to improve strength, especially surface strength, and to impart smoothness. Other film-forming materials which can be used for surface sizing include carboxymethyl cellulose (CMC) and poly(vinyl alcohol) (PVOH) which provide oil and grease repellent coatings, improve paper strength and decrease paper porosity. Other polymeric sizing agents such as polyurethanes and styrene-maleic anhydride copolymers (SMAs) are used as surface-sizing and strength-enhancing agents, but their cost is relatively high compared with other sizing agents (Dulany et al., 2011).

6.2.3.3   Barrier Coatings

Paper and paperboard are poor barriers to gases and water vapor. For example, a sized commercial kraft (54% pine and 46% eucalyptus) linerboard of 200 gsm has a water vapor transmission rate (WVTR) at low humidity (50% RH/23°C) of 426 g m^{-2} day^{-1} (Kugge and Johnson, 2008). Therefore, in many packaging applications, a barrier may be needed against water vapor or gases such as O_2. A water barrier can be formed by changing the wettability of the paper surface with sizing agents. Coating the paper with a continuous film of a suitable material will confer gas or vapor barrier properties.

Paraffin wax is low in cost, resists water vapor and is free of color, odor, taste or toxicity. It is applied by passing the paper through a molten bath or nip, removing the excess paraffin and cooling rapidly on a chill roll so that the wax forms a glossy surface. Modifiers, for example, microcrystalline wax, LDPE or EVA copolymer can improve the durability and film strength, raise the softening point and increase the gloss and heat seal strength of the coating (Hubbe, 2005). The main disadvantage with wax coatings is the difficulties associated with recycling of the paperboard, because the wax must be separated from the fibers so that they can be repulped. Wax has been largely replaced by LDPE applied by extrusion coating which results in a more durable and flexible coating that can be heat sealed to itself and is easily removed in a hydrapulper (see Section 5.3.2).

In theory, there is no reason why any thermoplastic which is normally processed by extrusion techniques cannot be coated onto paperboard. In practice, most extrusion coating technology that has been developed utilizes LDPE, although PP, PAs and PET are also used. For example, PET-coated paperboard is used in dual ovenable trays, where a 38 μm PET coating is put on 500–625 μm boardstock.

An increase in the water resistance of paperboard by coating it with PLA was reported by Rhim et al. (2007). When the coating thickness was varied from 4.7 to 42.7 μm, the water vapor permeability measured at 25°C/50% RH decreased from 4.8 to 25.5 times, while the water absorptiveness measured at 20°C decreased from 11.9 to 17.9 times. An optimum concentration of coating solution for improving water resistance of paperboard was 3 w/v% which gave a coating thickness of 28 μm

equivalent to 49.5 gsm. The moisture barrier and heat sealability properties of PLA extrusion coated paperboard (20 gsm) were reported by Lahtinen et al. (2009) who also presented a simple equation enabling calculation of the WVTR as a function of PLA coating weight at 23°C, 30°C and 38°C and 50%–90% RH.

Andersson (2008) and Aulin and Lindstrom (2011) reviewed recent developments of functional materials to improve the barrier properties of paperboard with particular emphasis on biobased polymers including starch and cellulose derivatives, chitosan, alginate, wheat gluten, whey proteins, polycaprolactone, PLA and polyhydroxyalkanoates. Their processability, convertibility, recyclability and biodegradability were discussed with a focus on novel application techniques. Khwaldia et al. (2010) reviewed the barrier, mechanical and other properties of biopolymer-coated paper and discussed existing and potential applications for bioactive coatings on paper packaging materials. These biopolymer coatings may retard unwanted moisture transfer in food products, are good O_2 and oil barriers, are biodegradable and, in their view, have potential to replace current petrochemical-based coatings. Han et al. (2010) reported on the use of two types of bilayer coating systems on paperboard (bees wax and either whey protein isolate (WPI)/cellulose film or poly(vinyl butyral) (PVB)/zein). The BW-PVB/zein bilayer system was more efficient than the BW-WPI/cellulose film bilayer system, with a strong reduction in WVTR of 95% as compared to uncoated paperboard. The WVTR of the BW-PVB/zein bilayer approached the desired industrial requirement for paperboard-based food containers of 10 g m^{-2} day^{-1}.

Perfluorochemicals and fluorochemicals are used in paper coatings for oil and moisture resistance in microwave popcorn bags, and fast-food paper packaging for muffin and french-fry bags, sandwich/burger wrappers and small pizza and burger boxes (Begley et al., 2008). The perfluorocarbon moiety in these classes of products has the effect of lowering the surface energy of the individual paper fibers which greatly contributes to the holdout of low surface energy liquids such as greases and oils. Begley et al. (2008) reported that fluorochemical paper additives migrate to food during actual package use. For example, microwave popcorn contained 3.2 mg fluorochemical kg^{-1} popcorn after popping. Residual perfluorooctanoic acid (PFOA) concentrations in the paper coatings result from reactions of starting materials, while fluorotelomer alcohols are actual starting ingredients in some formulations such as DuPont's Zonyl® RP used to produce the fluorochemical paper additive. The human body breaks down fluorotelomers into PFOA that accumulates in the human body.

A major shift in industrial fluorochemical production occurred in 2000, when 3M, the major manufacturer of perfluorochemicals, began phasing out its PFOA materials.

In 2007, DuPont announced that it had successfully commercialized a new, patented manufacturing process (termed LX platform) to remove greater than 97% of trace levels of PFOA, its homologues and direct precursors from its fluorotelomer products. DuPont also announced its commitment to eliminate the need to make, buy or use PFOA by 2015. Trier et al. (2011) have given a very informative update on polyfluorinated surfactants used to coat paper and board for food packaging, including analytical names, trade names, uses, suppliers and structures.

Recently, Jinkarn et al. (2012) showed that sulfur hexafluoride (SF_6) plasma treatment of paperboard surfaces can improve water resistance properties significantly, beginning with only a 2 s treatment time; oil resistance properties can be improved with a longer treatment time. Plasma treatment had no effect on tensile strength of treated paperboard; however, machine direction (MD) compression strength, as well as MD and cross direction (CD) folding endurance of treated paperboard was significantly lower than that for an untreated sample. The WVTR and OTR of treated paperboard were higher with increasing treatment time, because of etching of cellulose fibers caused by fluorine atoms and electron bombardment.

Barrier properties can be enhanced by incorporation of nano-sized materials in the coating. Nanocomposites are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. Extrusion coating was used to obtain MMT/LDPE-coated paperboard (Krook et al., 2005). The WVTR measured at 23°C/100% RH was essentially independent of

clay content and close to that of LDPE. The powerful melt mixing in the extrusion coating process triggered the separation of the clay stacks into small, evenly distributed entities. It also seemed that the same process yielded voids and pinholes that negatively affected the barrier properties.

A nano-structured copolymerized coating using high shape factor engineered (HSFE) clays that reduced permeation via a tortuous path was developed by Pal et al. (2008) for solid bleached sulfate (SBS) paperboard. The WVTR of the copolymerized acrylic coatings (2-ethylhexyl acrylate and methyl methacrylate) were reduced up to five times compared to the untreated baseboard with coating weights up to 20 gsm. The effects of pigment shape, baseboard, coat weight, calendering, RH and temperature on barrier properties were studied. The board samples showed almost zero gas permeability and a significant reduction of up to 90% in WVTR.

The use of micro-fibrillated cellulose (MFC) as a surface layer on base paper to significantly increase the strength of paper sheets and reduce their gas permeability dramatically was discussed in Section 3.3.5.2.3 Hult et al. (2010) deposited MFC and shellac on fiber-based substrates using a bar coater or a spray coating technique. The OTR decreased by several logarithmic units and the WVTR reached values considered as high barrier in food packaging (6.5 g m^{-2} day^{-1}). It was suggested that the utilization of a combined MFC and shellac coating on paper could be a viable alternative in the search for sustainable packaging. A pilot plant to produce MFC-coated liquid paperboard commenced production in Finland in 2012.

An alternative to extrusion coating is dispersion coating which has several advantages, including higher machine speeds and fewer processing stops than in the case of extrusion coating. Barrier dispersion coatings are typically compostable, less expensive and easier to apply.

An exciting new technique is atomic layer deposition (ALD) which was discussed in Chapter 5 Section 5.5.3. Hirvikorpi et al. (2010) studied the influence of corona pretreatment on the O_2 and water vapor barrier performance of polymer-coated paperboards additionally coated at 100°C with Al_2O_3 and SiO_2 by ALD. The effect of corona pre-treatment was negligible or even negative on the water vapor barrier, especially with the PLA-coated board.

6.2.3.4 Pigments

Though functionally and chemically similar, fillers and pigments are distinguished from one another in that fillers are added at the wet end of the paper machine and serve to fill the sheet; pigments are added at the size press and serve to alter the surface of the sheet.

Pigments comprise 70%–90% of the dry solids in paper coatings and are generally designed to mask or change the appearance of the base stock, improve opacity, impart a smooth and receptive surface for printing or provide special properties for particular purposes. The primary function of the adhesive in pigment coating is to bind the pigment particles together and to the raw stock. The type and proportion of the adhesive controls many of the characteristics of the finished paper such as surface strength, gloss, brightness, opacity, smoothness, ink receptivity and firmness of the surface. The strength must be sufficient to prevent the coating from being picked up by tacky printing inks (Hubbe, 2005).

The pigments which are used in paper coatings are similar to the materials that are used for paper, with kaolin clay being the largest-volume pigment for this application, followed by calcium carbonate. Plastic pigments based on PS are used in combination with mineral pigments to improve the gloss of coated papers (Dulany et al., 2011).

6.2.4 Physical Properties

Most properties of paper depend on direction. Paper has a definite grain caused by the greater orientation of fibers in the direction of travel of the paper machine, and the greater strength orientation that results partly from the greater fiber alignment and partly from the greater tension exerted on the paper in this direction during drying. The grain direction is known as the *machine direction* (MD), while the *cross direction* (CD) is the direction of the paper at right angles to the

MD. The grain of paper must be taken into account in measuring all physical properties. Most of the physical properties of paper depend on direction, that is, the MD, CD and thickness direction (z-direction) and these must be clearly indicated when reporting test results (Hubbe, 2005). An excellent review on the physics of paper was made by Alava and Niskanen (2006).

Papers vary in MD:CD strength ratios, with cylinder machine papers having a higher ratio than Fourdrinier papers, the latter values varying from about 1.5 to 2.5 (Hubbe, 2005). Usually, there is less variation in paper properties in the MD than in the CD because variations occur slowly in the MD, whereas in the CD they may occur quite suddenly for a variety of process-related reasons. In addition, the CD strength normally varies depending on how far the sample was taken from the edge of the sheet. In general, papers should be used to take greatest advantage of the grain of the paper.

6.2.5   Types of Paper

Paper is divided into two broad categories: (1) fine papers, generally made of bleached pulp, and typically used for writing paper, bond, ledger, book and cover papers, and (2) coarse papers, generally made of unbleached kraft softwood pulps and used for packaging.

6.2.5.1   Kraft Paper

Kraft paper is typically coarse with exceptional strength, often made on a Fourdrinier machine and then either machine-glazed on a Yankee dryer or machine-finished on a calender. It is sometimes made with no calendering so that when it is converted into bags, the rough surface will prevent them from sliding over one another when stacked on pallets.

6.2.5.2   Bleached Paper

Bleached paper is manufactured from pulps which are relatively white, bright and soft and receptive to the special chemicals necessary to develop many functional properties. It is generally more expensive and weaker than unbleached paper. Its aesthetic appeal is frequently augmented by clay coating on one or both sides.

6.2.5.3   Greaseproof Paper

Greaseproof paper is a translucent, machine-finished paper which has been hydrated to give oil and grease resistance. Prolonged beating or mechanical refining is used to fibrillate and break the cellulose fibers which absorb so much water that they become superficially gelatinized and sticky. This physical phenomenon is called hydration and results in consolidation of the web in the paper machine with many of the interstitial spaces filled in.

The satisfactory performance of greaseproof papers depends on the extent to which the pores have been closed. Provided that there are few interconnecting pores between the fibers, the passage of liquids is difficult. However, they are not strictly "greaseproof" because oils and fats will penetrate them after a certain interval of time. Despite this, they are often used for packaging butter and similar fatty foods since they resist the penetration of fat for a reasonable period.

6.2.5.4   Glassine Paper

Glassine paper derives its name from its glassy, smooth surface, high density and transparency. It is produced by further treating greaseproof paper in a supercalender where is it carefully dampened with water and run through a battery of steam-heated rollers. This results in such intimate interfiber hydrogen bonding that the refractive index of the glassine paper approaches the 1.02 value of amorphous cellulose, indicating that very few pores or other fiber/air interfaces exist for scattering light or allowing liquid penetration (Paper, 2009). The transparency can vary widely depending on the degree of hydration of the pulp and the basis weight of the paper. The addition of titanium dioxide makes the paper opaque, and it is frequently plasticized to increase its toughness.

6.2.5.5   Vegetable Parchment

Vegetable parchment takes its name from its physical similarity to animal parchment (vellum) which is made from animal skins. The process for producing parchment paper was developed in the 1850s, and involves passing a web of high quality, unsized chemical pulp through a bath of concentrated sulfuric acid. The cellulosic fibers swell and partially dissolve, filling the interstices between the fibers and resulting in extensive hydrogen bonding. Thorough washing in water, followed by drying on conventional papermaking dryers, causes reprecipitation and consolidation of the network, resulting in a paper that is stronger wet than dry (it has excellent wet strength, even in boiling water), free of lint, odor and taste, and resistant to grease and oils (Paper, 2009). Unless specially coated or of a heavy weight, it is not a good barrier to gases.

Because of its grease resistance and wet strength, it strips away easily from food material without defibering, thus finding use as an interleaver between slices of food such as meat or pastry. Labels and inserts in products with high oil or grease content are frequently made from parchment. It can be treated with mold inhibitors and used to wrap foods such as cheese.

Parchment paper with great shock-absorbing capability can be produced by wet creping, resulting in extensibility combined with natural tensile toughness. Special finishing processes provide qualities ranging from rough to smooth, brittle to soft and sticky to releasable. It was first used for wrapping fatty foods such as butter, an application still used today.

Glazed imitation parchment (GIP) is made from strong sulfite pulp, which is heavily engine-sized and glazed to give the necessary degree of protection.

6.2.5.6   Waxed Paper

Waxed papers provide a barrier against penetration of liquids and vapors. Many base papers are suitable for waxing, including greaseproof and glassine papers. The major types are wet-waxed, dry-waxed and wax-laminated. Wax-sized papers, in which the wax is added at the beater during the papermaking process, have the least amount of wax and therefore give the least amount of protection.

Wet-waxed papers have a continuous surface film on one or both sides, which is achieved by shock-chilling the waxed web immediately after application of the wax. This also imparts a high degree of gloss on the coated surface. Dry-waxed papers are produced using heated rollers and do not have a continuous film on the surfaces. Consequently, exposed fibers act as wicks and transport moisture into the paper. Wax-laminated papers are bonded with a continuous film of wax that acts as an adhesive. The primary purpose of the wax is to provide a moisture barrier and a heat sealable laminant. Frequently, special resins or plastic polymers are added to the wax to improve adhesion and low temperature performance and to prevent cracking as a result of folding and bending of the paper. However, replacement of wax coatings by thermoplastics is a continuing trend.

6.3   PAPERBOARD PRODUCTS

Paper is generally termed board when its grammage exceeds 250 gsm. Various types of paperboards are manufactured, and a partial listing of paperboard grades is given in Table 6.1. Boards can be manufactured in a single Fourdrinier wire, a single cylinder former or on a series of formers of the same type or combination of types (Smook, 2002).

Multi-ply boards are produced by the consolidation of one or more web plies into a single sheet of paperboard which is then subsequently used to manufacture rigid boxes, folding cartons, beverage cartons and similar products. One advantage of multi-ply forming is the ability to utilize inexpensive and bulky low grade waste materials (mostly old newspapers and other postconsumer waste papers) in the inner plies of the board where low fiber strength and the presence of extraneous materials (e.g., inks, coatings, etc.) have little effect on board properties (Smook, 2002). However, multi-ply boards containing postconsumer waste papers should not be used for food contact purposes.

TABLE 6.1
Paperboard Grades

Linerboard—board having at least two plies, the top layer being of relatively better
  quality; usually made on a Fourdrinier machine with 100% virgin pulp furnish
Foodboard—board used for food packaging having a single-ply or multi-ply
  construction, usually made from 100% bleached virgin pulp furnish
Folding boxboard—multi-ply board used to make folding boxes; middle plies are made
  from mechanical pulp sandwiched between two layers of virgin chemical pulp
Chipboard—multi-ply board made from 100% recovered (secondary) fiber
Baseboard—board that will ultimately be coated or covered

6.3.1 Folding Cartons

Folding cartons are containers made from sheets of paperboard (typically with thicknesses between 300 and 1100 µm) which have been cut and scored for bending into desired shapes; they are delivered in a collapsed state for erection at the packaging point (Obolewicz, 2009).

The boards used for cartons have a ply structure and many different structures are possible, ranging from recycled fibers from a variety of sources (as in chipboards), through fibers where the outer ply is replaced with better quality pulps to give white-lined chipboards, to duplex boards without any waste pulp and solid white boards made entirely from bleached chemical pulp. The most widely used types of paperboard are as follows:

1. *Coated Solid Bleached Board (SBB) or Solid Bleached Sulfate (SBS)*: this grade is typically made from pure bleached chemical pulp with two or three layers of coating on the top surface and one layer on the reverse. It is used for chocolate confectionary, cheese, coffee, tea, reheatable products and frozen foods (Robertson, 2012). It can also be combined with SUB and other materials to make liquid packaging board (LPB).
2. *Coated Solid Unbleached Board (SUB) or Solid Unbleached Sulfate (SUS)*: this is 100% virgin, unbleached, chemical furnish and typically has two to three layers of mineral or synthetic pigment coating on the top and one layer on the reverse side. It is also known as Coated Unbleached Kraft (CUK). Recycled fibers are sometimes used to replace the unbleached chemical pulp. The primary reason for coating unbleached or natural kraft paperboard with a thin layer of kaolin clay is to improve its printing surface.
3. *Folding Box Board (FBB)*: This grade is typically made from middle layers of mechanical pulp sandwiched between two layers of chemical pulp with up to three layers of coating on the top or printing surface and one layer of coating on the reverse. The mechanical pulp gives high stiffness with high bulk and the chemical pulp gives high strength. It is used for products such as drinks, confectionery, frozen and chilled foods, tea, coffee, bakery products and cookies/biscuits.
4. *White Lined Chipboard (WLC)*: This grade is typically made using predominantly recovered fibers. It is manufactured in a number of layers each of which use selected grades of raw materials. It typically has two or three layers of coating on the top or printing surface which consists of bleached chemical pulp. The second layer is made of bleached chemical or mechanical pulp while the middle layers (commonly three in total) are unbleached recycled pulp from mixed paper or carton waste. The bottom or inside layer is specially selected recycled pulp (underliner). Some uncoated paperboard is produced with a top ply of white recovered fiber. WLC is used in a range of applications such as frozen and chilled foods, dried food and breakfast cereals.

In the absence of a functional barrier, mineral oil hydrocarbons (MOHs) from printing inks and recycled fibers tend to migrate from paper-based food packaging materials through the gas phase into dry food. Concentrations exceed the limit derived from the ADI by a factor of up to 100. The main sources of mineral oil in paperboard are offset printing inks, either directly applied for decorating the food packaging material or entering via recycling of fibers contaminated by mineral oil-containing inks, primarily from newspaper. The contamination of powdered baby milk and other dry foods packed in cardboard boxes over several weeks with MOHs at concentrations of 10–150 mg kg^{-1} was first reported in 1997; internal paper bags with a plastic layer did not stop the migration. The migration of MOHs threatens the use of paperboard made of recycled fibers for food packaging. As a short-term measure, the mineral oil content could be reduced through the selection of the paper and board fed into the recycling process. The most favorable starting materials available in sufficient amount, such as corrugated board, might reduce the concentration of the migrating mineral oil by a factor of 5, but the ADI would still be exceeded by up to 20 times. To meet the legal limit, a total elimination of mineral oil from offset printing inks (not only in newspapers but also in other printed matter) has been suggested (Biedermann et al., 2011). This topic is discussed further in Section 22.5.4.

A number of steps are involved in converting paperboard into cartons. Where special barrier properties are required, coating and laminating are carried out. Wax lamination provides a moisture barrier, lining with glassine provides grease resistance and laminating or extrusion coating with plastic materials confers special properties including heat sealing. The use of barrier materials in cartonboard is restricted by the inability of the normal types of carton closure to prevent the ingress of moisture directly.

Coating of the outer board greatly enhances the external appearance and printing quality, and clay and other minerals are used for such purposes. The coating can be applied either during the board-making operation or subsequently. Foil-lined boards are also used for various types of cartons, to (in certain applications) improve reheatability of the contents.

The conventional methods of carton manufacture involve printing of the board, followed by creasing and cutting to permit the subsequent folding to shape, the stripping of any waste material which is not required in the final construction, and the finishing operation of joining appropriate parts of the board, either by gluing, heat sealing or (occasionally) stitching. During creasing and folding, cartonboard is subjected to complex stresses, and the ability of a board to make a good carton depends on its rigidity, ease of ply delamination and the stretch properties of the printed liner. It is important that the surface layer on the top of the board is of an elastic nature and relatively high strength compared with the properties of the underlying layers since they will be in compression.

An exciting new development is 3D forming of paperboard (Hauptmann and Majschak, 2011). Although still only at the first stage of R&D, it promises to revolutionize paperboard packaging if successfully commercialized.

6.3.2 BEVERAGE CARTONS

The first records of paper being used to carry liquids on a commercial scale are found in reports, dated 1908, of a Dr Winslow of Seattle. He remarked on paper milk containers which were invented and sold in San Francisco and Los Angeles by a G.W. Maxwell as early as 1906. Paraffin wax was used to moisture proof the paper but achieving a liquid-tight bond at the joins was more difficult. In 1915, John Van Wormer, owner of a toy factory in Toledo, Ohio was granted a U.S. patent for a "paper bottle" (actually a folded blank box) for milk that he called Pure-Pak. The crucial and unique feature was that this box would be delivered flat to be folded, glued, filled and sealed at the dairy. This offered significant savings in delivery and storage in comparison with preformed glass bottles, then the predominant package for milk, having being introduced in 1889. The challenge came with the design of the machinery to be sold or leased to the dairy to form, fill and seal the cartons. The detailed development history of the paper beverage carton has been described by Robertson (2002).

The carton normally consists of layers of SBB and (outside North America and Japan) SUB coated internally and externally with LDPE, resulting in a carton which is impermeable to liquids and in which the internal and external surfaces may be heat sealed. There may also be a thin layer of aluminum foil, which acts as a gas and light barrier. The structure and functions of the various layers in an aseptic paperboard carton are described in Section 13.3.1.

The modern gable top carton retains the simple basic geometry of earlier years although flat-topped and plastic-topped versions are available (Lisiecki, 2009). Added refinements such as plastic screw caps and reclosable spouts are also available. Incorporation of an aluminum foil layer permits longer shelf life of chilled premium juice products; in some cases, the foil is replaced by a barrier polymer such as EVOH or SiO_x-coated PET. If the foil is replaced, then the carton must be sealed using ultrasonic sealing or heated jaws rather than induction sealing.

Liquid-tight, hermetically-sealed brick-shaped cartons are widely used for the aseptic packaging of a wide range of liquid foods including milk, juices, soups and wines to give packs which will retain the product in a commercially sterile state for years. The end of shelf life (typically 6–9 months) is determined by organoleptic changes as a result of undesirable chemical and physical reactions. In 2011, the Tetra Evero 1L aseptic carton bottle (billed as the world's first) for white milk was launched. It consists of the standard aseptic paperboard-foil-plastic body with an injection molded plastic cap and top.

A blank-fed, retortable, square-shaped paperboard carton for soups, ready meals, vegetables and pet food has been commercialized as a replacement for the metal can and a competitor for the retort pouch; it is known as Tetra Recart. Of basically similar structure to the aseptic carton (see Chapter 13) but with PP replacing LDPE, products packaged in it have a shelf life under ambient conditions of 18 months.

In recent years, there has been considerable publicity about the development of paper bottles. The GreenBottle® in the United Kingdom consists of a molded pulp outer with an inner plastic pouch complete with screw cap. The Ecologic Brands paper bottle in California consists of a molded pulp outer shell and an inner plastic pouch made from LDPE with a patented resealable spout made from PP. Both packages are basically bag-in-box technology: a paperboard shell for rigidity with an LDPE internal pouch to hold the product. The 360 Paper Water Bottle is a single serve water bottle made from sustainable sheet stock such as bamboo, palm leaves, etc. An internal PLA film provides the liquid barrier and enables the two pressed halves to be sealed. Rather than being unscrewed, the bottle features a lid which peels off into two pieces: one piece keeps the top clean from dust or other contaminants and the other can be reattached to seal the bottle. The design enables the self-bundling of multiple containers to eliminate the need for separate six pack packaging.

6.3.3 Molded Pulp Containers

The term "molded pulp" is used to describe 3D packaging and food service articles that are manufactured from an aqueous slurry of cellulosic fibers and formed into discrete products on screened molds (Waldman, 2009). Typically, the raw materials consist of virgin mechanical and chemical wood pulp, and waste paper pulps with or without the addition of the former materials.

The forming process is similar in many ways to the paper-making process, except that a mold fitted with a screen is used in place of the moving wire screen. Two molding processes are used. In the pressure injection process, air under pressure and at a temperature of approximately 480°C is used to form a pulp and water mixture in a mold. This process is semiautomatic and moldings have a thicker and variable wall thickness; it is less suitable for producing more complicated designs and has been largely superseded by the suction molding process in which the pulp mixture is pumped into a perforated mold where water is removed by a partial vacuum. The molded item is then dried.

Typical uses of pressure-molded containers include the packaging of bottled wines and spirits where a pulp sleeve molded to the profile of the glass bottles enables them to be packed head to tail in a carton, thus saving a considerable amount of space. Well-known forms of molded pulp articles

made by the suction-molding process include egg cartons, food trays and many other forms of tray-shaped articles for packing fruit and other commodities. Thin thermoplastic films such as PET can be laminated to one surface of a molded pulp tray, enabling it to function as a dual ovenability container (i.e., suitable to be used in microwave and convection ovens) for such products as frozen dinners.

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