PAPER

1. Introduction

1.1. Definition and History. Paper is a sheet material comprised of individual fibers that are brought together by the removal of water on a screen fabric or a between a pair of such fabrics. The first recorded account of paper that meets the definition just given was from ancient China. It is recorded that in the year 105 AD, Cai Lun, a courtier serving the emperor of the Han dynasty, made significant advances in the strength and quality of paper sheets.

Early accounts of paper describe its preparation from a variety of materials, including fibers from the inner bark of the paper mulberry tree. Ancient paper also was prepared from cast-off textile fibers, making paper the oldest known product prepared from recycled materials. Handcraft papermakers continue to use fibers from such plants as flax, hemp, cotton, and a variety of grasses. A common feature of all such fibers is that they contain cellulose, a natural polysaccharide (see CELLULOSE). The polysaccharide molecules provide typical papermaking fibers with a water-loving character. Once the fibers have been liberated from each other, they are readily dispersible in aqueous solution.

Though the word paper is derived from the word papyrus, the two products have different origins. Papyrus was developed in ancient Egypt. Unlike paper, the process of forming papyrus sheets does not involve individualized fibers. Rather, flat reeds of the *Cyperus papyrus* species are pounded repeatedly to make them flexible (1). The softened reeds then are pressed together into crisscross layers and dried.

During the middle ages in Western lands the use of papyrus was generally abandoned in favor of parchment, derived from leather. Meanwhile, the ancient technology of papermaking, long kept as a trade secret of the ancient Chinese, gradually began to spread (2). The manufacture of paper from bark and bamboo spread from China to Japan, where its manufacture began in about the year 610. Papermaking from flax and hemp spread through Central Asia, the Middle East, and eventually into Europe. The first European paper was made in Spain in 1150, in France by 1189, in Germany by 1320, and in England by 1494. Papermaking was introduced in the United States in ~1700 by William Rittenhouse in Philadelphia (3).

In light of the fact that the vast majority of modern paper is prepared from wood fibers, it is perhaps surprising that such technology did not arise until the mid-1800s (2). The relative lateness of wood's emergence as a major fiber source for paper probably can best be explained by the very strong and chemically resistant lignin that joins fibers together in natural wood. Lignin is a natural, cross-linked phenolic resin. Papermakers have used basically two kinds of approaches to separating the fibers, either applying drastic mechanical force or applying harsh chemical treatments to dissolve the lignin. These two approaches, as well as some technologies combining both approaches, are summarized in the section Manufacturing: Preparing Fibers for Papermaking.

1.2. Economic Impact of Paper. Based on tonnage, it might be said that paper is the world's most important manufactured item. Annual world production of paper and paperboard exceeds 330 million metric tons. The U.S. production in 2004 was ~92 million metric tons, of which ~42 million tons were classed as paper products and ~50 million tons were products heavy enough to be classed as paperboard (4). Within the paper category, the most important kinds of products, in order of decreasing amounts, were uncoated papers produced with chemical pulp (see the section Chemical Pulps), coated papers (see the section Pigment Coatings), newsprint (made mainly with mechanical pulp, see the section Mechanical Pulps for Papermaking), tissue, and packaging papers. Within the paperboard category the most important product groups, in order of decreasing amounts, were made from unbleached kraft pulp (see the section Mechanical Pulps for Papermaking), followed by recycled fibers, followed by semichemical pulp (see the section Mechanical Pulps with Chemical Treatment), and finally bleached pulp. The net production of paper and board products, both in the United States and other countries, generally has followed the gross national product. Not surprisingly, the highest recent rates of growth in paper production have been in China, as well as South American, southern Asia, and Indonesia.

Worldwide annual sales of paper and paperboard can be conservatively estimated as ~ \$200 billion, based on production rates, in combination with typical prices of the most widely produced grades (5). World production in the year 2000 included 39 million metric tons of newsprint paper, 99 of printing and writing papers, and 185 million metric tons of packaging and "other" paper and paperboard products. Prices of paper products fluctuate considerably, depending on supply and demand within different product groups. Typical prices per metric ton can range from ~ \$450 for recycled, coated boxboard, to ~ \$565 for commodity grade newsprint, to \$850 for copy paper. Also, one can expect to pay considerably more for tissue, cigarette paper, and various specialty grades.

The U.S. economic impact of paper and paperboard similarly can be estimated from production and market data. Paper production in 2004 included 11.3 million metric tons of uncoated free sheet, 8.3 of coated papers, 5.1 of newsprint, 6.4 of tissue, 3.7 of packaging and converting, and 2.7 of other paper grades. Paperboard in the same year included 20.6 million metric tons of unbleached kraft products, 13.7 of recycled board, 5.9 of semichemical board, and 5.1 of bleached board. Based on price estimates for some typical products within various categories, \$70 billion/year can be considered a conservative estimate of total U.S. sales.

In addition to the value of paper itself, the American Forest and Paper Association (AF&PA) estimated that mail and other paper-based industries provide >9 million U.S. jobs (6). Overall economic activity related to paper and paperboard was estimated to be \$850 billion/year. In 2000, North American mills produced ~30% of the world's production. The United States, representing ~4.6% of the world's population, consumes ~28% of the paper and board.

2. Chemical and Material Composition

The words *mixture* and *composite* are useful when describing the chemical composition of paper. With a few exceptions, which will be noted, paper's components do not become covalently bonded to each other during manufacture. Rather, the ingredients are mainly held together by reversible hydrogen bonds, in addition to

London dispersion forces. The reversible nature of the bonding can be demonstrated by soaking paper in water, followed by agitation, as in the case of a kitchen blender. Though paper's composition varies widely, depending largely on its intended use, key ingredients of typical paper products are cellulosic fibers, mineral products, and bonding agents, including starch and latex products. Other additives, which seldom individually make up $>1\%$ of paper's mass, include polyelectrolytes, inorganic coagulants, processing aids such as defoamers and biocides, as well as a variety of additives designed to impart functional characteristics to the paper.

2.1. Chemical Composition of Fibers. The fiber in typical paper can be called "cellulosic", meaning that cellulose [9004-34-6] is its most prominent component. Figure 1 shows cellulose's repeating molecular unit. Cellulose is present not only in wood, but also in various non-woody plants, such as straw, sugarcane (bagasse), reeds, and hemp. Cellulose is a polysaccharide, ie, a polymer comprised of sugar subunits. The stereochemistry of the six-carbon sucrose units that comprise cellulose, as well as the nature of the β-1,4 glycosidic linkages between those units, give rise to a unique tendency to form linear fibrous structures. Localized crystalline regions within these structures tend to be interposed by noncrystalline regions within the cell walls of the fibers.

Wood, the major source of cellulosic papermaking fibers, can likewise be described as a composite. Its four main solid ingredients are held together mainly by physical chemical forces, rather than by a high degree of covalent bonding between them. Three of the ingredients, cellulose, hemicellulose, and lignin, are polymeric. The fourth ingredient, the extractives portion of wood, is actually a class of monomeric resinous materials. Table 1 shows the relative proportions of ingredients for a typical hardwood (deciduous) and softwood (conifer) species used for papermaking.

The proportion of different types of fiber in paper depends on the intended use. Softwood fibers, having typical lengths of 2.5–4 mm, are desirable for products requiring high levels of tear, tensile, and fold strength, as well as resistance to edgewise compression forces. Products taking advantage of such attributes of softwood fibers include paper bags, as well as linerboard for corrugated containers. Premium towel and tissue papers are often comprised of softwood fibers. By contrast, hardwood fibers, having fiber lengths closer to 1 mm, are prized for applications demanding smoothness, as in the case of printing papers. To simultaneously achieve the strength, smoothness, and other specified properties of many grades of paper, it can be advantageous to employ blends of the two main categories of wood fibers, as mentioned.

Hemicellulose [9034-32-6] is a polysaccharide, like cellulose; however, its structure is more complicated and more varied. From the papermaker's perspective, hemicellulose can be considered as a natural "dry-strength agent" (see the section Dry-Strength Additives). Because of their various side groups, the hemicellulose molecules generally are unable to form the type of crystalline structure for which cellulose is noted. The dominant form of hemicellulose present in hardwood species is 4-*o*-methyl-D-glucuronoxylan [9062-57-1]. By contrast, the hemicellulose in softwood is mainly glucomannan [76081-94-2]. Examples of these polymers are shown in Fig. 2. The presence of carboxylic acid functions on glucose side-groups of the glucuronoxylans helps to explain a generally higher negative surface charge density of hardwood fibers, compared to softwood fibers prepared by similar pulping methods. The acid groups also contribute to the swelling of fibers in water. High correlations have been observed between the ability of fibers to swell in water, the compliance of their surfaces, and the development of bonds between them when paper is dried.

The third major component of papermaking fibers, especially prominent in natural wood and mechanical pulp fibers, is lignin [8068-05-1], which consists of naturally cross-linked phenol–propane units having a variety of ether, ester, and carbon–carbon bond connections between them. Lignin poses significant challenges for papermakers. Not only is lignin very difficult to chemically remove from fibers, but it also has a dark, unstable color.

The extractives component of wood includes a variety of fatty acid, triglyceride, and unsaponifiable organic compounds. In addition, mechanical fibers obtained from conifers, such as pine, can contain ∼1% by mass of resin acids, including levopimeric acid, abietic acid, and other terpenoids.

2.2. How Pulping Methods Affect Papermaking Fiber Chemical Properties. Differences in pulping methods, as well as in the tree species used as fiber sources result in large differences in the composition of fibers used for different paper products. There are two main ways of converting wood to dispersible fibers. Mechanical pulping uses mainly compressive and shearing forces to separate wetted fibers from the wood matrix. Chemical pulping dissolves the bonding material, ie, the lignin, which is then removed from the pulp by subsequent washing and optional bleaching steps.

Mechanical Pulps for Papermaking. Because there is little dissolution of wood components resulting from mechanical pulping, the process results in a high pulp yield, eg, 95%, and the chemical composition resembles native wood. Fiber separation is most often achieved by passing wood chips between a pair of metal surfaces, one of which is rotating. The metal surfaces, often in the shape of disks, are covered with patterns of raised, rectangular bars. Such devices, known as “refiners”, have largely replaced the use of grindstones for mechanical pulp production. Refiner mechanical pulp (RMP) is produced at atmospheric pressure from a disk refiner; it is the oldest of the refiner processes. In the thermomechanical pulping (TMP) process, wood chips are heated to ∼120°C with pressurized steam before and during refining. This is done to soften the wood chips and minimize damage to the fibers as they are released from the wood structure. Compared to stone groundwood pulp, TMP is comprised of longer, less damaged fibers and less debris, which results in improved strength, but some opacity loss. The TMP can be used to replace chemical pulp fibers in the fiber blends used to make some paper products. Softwood is the preferred raw material to produce high strength paper products. In the stone groundwood process, fibers are separated from the wood by grinding logs against revolving stone wheels. The resultant fibers are fractured and much fibrillar debris is generated. Mechanical pulps are used where opacity and good printability are needed. The presence of large amounts of lignin, however, results in lower interfiber bonding and tensile strength, as well as poor light stability. Such pulps may be bleached with sequences that maintain a high pulp yield and do not remove lignin. Typical bleaching chemicals are alkaline hydrogen peroxide and sodium hydrosulfite (dithionite). Brightness up to 80% can be easily achieved.

Mechanical Pulps with Chemical Treatment. Combinations of mechanical and chemical pulping methods can be used. For example, sodium sulfite and hydrogen peroxide can be added during TMP processing to achieve improved strength; such pulp is called chemithermomechanical pulp (CTMP). The strength improvements, which may be 50%, are obtained at some sacrifice to yield and opacity. The yields of chemimechanical pulps are 90–95%.

The next significant class of pulps, semichemical pulps, are produced by mild chemical digestion of wood chips, followed by passage through a disk refiner. Yields are generally <80%. The main use is in corrugated media for packing boxes. High stiffness, resulting from the relatively high lignin and hemicellulose levels, is a product advantage. Hardwoods usually are the base woods for semichemical pulps. Use of the neutral sulfite process is declining because of environmental problems, due to a lack of an efficient system for chemical recovery. Newer processes, which are based on sodium carbonate–sodium sulfide, ie, the green liquor process, or sodium hydroxide–sodium carbonate, are replacing the neutral sulfite sequence. Compared to the neutral sulfite pulps, these alkaline semichemical pulps are darker and have slightly more lignin. High yield unbleached kraft pulps (see next section) are also favored for production of corrugating medium.

Chemical Pulps. Chemical pulps have greatly reduced lignin contents compared to the native wood, as a result of dissolution during chemical digestion. Much less mechanical energy is needed to separate the fibers from the wood matrix, and the resulting fibers are relatively undamaged and strong. Chemical pulps are widely used for paper and paperboard products requiring high strength. In addition, modern bleaching practices make it possible to convert the fibers from a brown or tan shade to high levels of brightness, rendering the fibers suitable for fine printing paper.

Kraft is the dominant process for producing chemical pulps. Yields are typically 46–56%. The higher yield kraft pulps, containing ~10% lignin, are used especially for linerboard (see the section Paperboard Trades). Lower yield pulps typically are bleached to remove virtually all lignin and to produce high brightness (90%+). Although the most widely used chemical processes for pulping and bleaching can be described as “selective”, preferentially breaking down and dissolving lignin, rather than cellulose, significant loss of cellulose macromolecular chain length does occur. For example, the degree of polymerization (DP) may decrease from ~9000, in the case of natural wood, down to ~6000, in the case of a typical unbleached kraft fiber for containerboard, and further down to ~4000, in the case of a relatively low yield, bleached kraft pulp intended for printing paper (7). Fortunately, the relation between paper strength and cellulose DP is not strong.

Summary of Fiber Composition and Physical Attributes. Table 2 shows typical examples of the chemical content of widely used mechanical and chemical pulps used by papermakers. Note that the word “yield” denotes the mass percentage of the original solid wood that is retained in the fibers.

The chemical differences between types of papermaking fibers, as illustrated in Table 2, can impact both the process and the product of papermaking. The extractives components, which are especially prevalent in TMP and high yield kraft pulps, eg, generally can be described as water hating. A fraction of the extractives may become solubilized or emulsified during the papermaking process, and some of this same material may later precipitate as “pitch” deposits on the papermaking equipment. Alternatively, agglomerated pitch can show up as discolored blemishes in the product. To combat such problems, papermakers employ a variety of strategies, including seasoning of wood chips, addition of dispersed talc to the pulp, coagulation of pitch droplets onto fibers by addition of aluminum sulfate, and various surface treatments of processing equipment. The resin acid component from softwood fibers tends to increase the water-repellent nature of paper, especially when soluble aluminum compounds are present.

Differences in lignin content also affect paper properties. For example, papermakers use relatively noncompliant mechanical fibers to advantage in such products as newsprint, where the opacity of the paper is critical. The irregular shapes of a mechanical pulp produce efficient light scattering, due to the many air spaces within the resulting paper sheet. By contrast, kraft fibers, which are more compliant and bondable, tend to produce denser, more translucent paper (except, see the section Fillers). Relatively high lignin content also is favored for paperboard products that required a high resistance to edgewise crush.

Chemical analyses used to characterize wood pulps for papermaking include determinations of α-, β-, and γ-cellulose, carbohydrates, lignin, carboxyl and carbonyl groups, copper number, and viscosity. The carbohydrate determination involves acid hydrolysis of the pulp, preparation of volatile derivatives, and separation of the individual monomeric sugars by gas chromatography (see TAPPI T249 and ASTM D1915). Results are used to compute percentages of cellulose and hemicellulose in the pulp. Lignin can be defined as that portion of the pulp that is insoluble in 72 wt.% sulfuric acid (see TAPPI T223 and ASTM D1106). The α-, β-, and γ-cellulose test (TAPPI T203) and other determinations based on alkali solubility (TAPPI T212 and T235, ASTM D1696) reflect empirically the hemicellulose content of the sample and the degradation of the cellulose. Also indicative of hydrolytic or oxidative degradation of the pulp are higher carboxyl (TAPPI T237 and ASTM D1926), carbonyl, and copper number values and lower viscosity. Cupriethylenediamine or lithium salt solutions of cellulose are used for the viscosity tests (TAPPI T254 and ASTM D539); results are related to the average degree of polymerization.

2.3. Recovered Fibers. Due to significant recycling of paper, reclaimed fiber accounts for almost one-half of the total papermaking fiber used in the United States. Recovered paper is often collected or sorted into the following categories:

Old newspaper (ONP) pulp is mainly comprised of mechanical pulp fibers, such as TMP (see the section Mechanical Pulps for Papermaking). When the recovered materials are repulped (see the section Stock Preparation), wetting agents and heat may be added to the water to promote separation of the fibers. The ONP usually contains substantial amounts of ink, which can be removed by process steps that including floatation deinking.

Old corrugated container (OCC) pulp, which is mainly from used shipping boxes, usually is comprised of unbleached softwood and hardwood kraft pulps. Significant amounts of starch adhesive, used in sealing the boxes, may also be present. High grade ONP is sometimes designated as DLK, standing for "double-lined kraft". The presence of wax, wet-strength treatments (see the section Permanent Wet-Strength Resins), and various glossy print layers in certain corrugated boxes can present challenges for recycling.

Mixed office waste (MOW) pulp is comprised mainly of bleached kraft fibers, except that the collected material is usually contaminated by printing inks, xerographic toners, plastic from inserts and envelope windows, pressure-sensitive adhesives, and various other minor ingredients. Deinking of MOW yields substantial amounts of sludge, of which mineral filler, inks, deinking chemical residues, and products of biological wastewater treatment are often the main components. Typical yields for deinking processes range from 60 to 80%.

Premium recovered fibers, from the standpoint of the papermaker, can include envelope clippings and similar paper scraps that never get touched by consumers. Such fiber sources have been in high demand by papermakers for many years, long before the development of modern deinking methods.

Compared to wood-derived fibers, nonwood cellulosic fibers are used in relatively small volumes. Exceptions to this rule include the use of bagasse fibers from sugarcane in sugar-producing regions. Also, straw has been widely used in China, due to a relative lack of forest resources. Other examples of nonwood pulps and products include cotton linters for writing paper and filters, esparto for filter paper, bagasse for corrugated media, and Manila hemp for tea bags.

2.4. Non-Cellulosic Fibers Used by Papermakers.

The term "wet-laid nonwovens" is often used to describe paper that contains substantial amounts of non-cellulosic fibers. Synthetic pulps used in wet-laid products include glass fibers, polyolefins, polyesters, and various specialty fibers such as carbon fibers. Synthetic fibers are often used in blends with wood fibers, where they contribute to properties such as tear resistance, stiffness, or wet strength, depending on what is needed to meet customer requirements. Some familiar wet-laid products are hospital gowns, automotive filters, brake linings, and composites used in high performance aircraft construction.

The manufacture of wet-laid products is practically identical to ordinary papermaking. Certain modifications to the process, as follows, are often used in order to deal more effectively with relatively long synthetic fibers that lack the ability to bond to each other when they are dried.

The solids content of the fibrous slurry, just before formation of the continuous sheet, can be substantially lower (eg, 0.05–0.5%), compared to conventional paper with wood-derived fibers (eg, 0.3–1.5%).

Special designs of paper machine forming sections, including single-fabric machines with inclined tables, can be used in order to deal with the needed large quantities of dilution water.

Papermakers often add an excess of high mass water-loving polyelectrolytes, such as acrylate copolymers, to the water to minimize tangling of relatively long synthetic fibers.

In cases where the recipe includes no cellulosic fibers, it is common to pass the wet web through a saturating bath of adhesive resin before the product is dried. Alternatively, binding materials, including latex, may be sprayed onto the surface or applied as a foam layer.

2.5. Fiber Identification in Paper. The ratio between different fiber types is often a key to achieving favorable paper properties for a given application. Qualitative and quantitative methods have been developed to determine the fibrous constituents in a sheet of paper (see 20, 23, TAPPI T401). A common method involves tearing a representative sample into small pieces, boiling them in dilute sodium hydroxide, and repeated washing, followed by vigorous shaking to disperse the fibers. Stains are used to reveal the pulping process and to produce contrast for the identification of the fibers by microscope. Graff's C stain is probably the best stain for general fiber analysis. Other stains used are Wilson's stain, Herzberg stain, and the Green-Yorston stain (AZO). The colors that are developed by these stains vary according to the raw material used and the pulping process.

2.6. Nonfiber Ingredients of Paper and Their Chemistry. Depending to a large extent on the intended use of a paper product, the fiber proportion can vary within the range of ~50 and 96% of its mass. This is a broad range mainly because some paper products contain substantial proportions of mineral, whereas some other paper products do not. Aqueous suspensions of mineral particles either can be added to the fiber slurry, before the paper is made, or they can be applied as part of a coating on one or both surfaces of an existing sheet.

2.7. Water Content of Paper Products. The dry fiber content of paper products, by mass, is seldom >96%, because water is the only other ingredient, besides fibers, that is present in significant amounts in essentially every type of paper. As it is manufactured, paper typically has a water content within the range of 4–8%, roughly matching the expected equilibrium moisture content under typical conditions of relative humidity.

Water versus Paper's Dimensional Stability. Because fibers tend to swell in their thickness direction with increasing relative humidity, there is a potential for dimensional instability, curl problems, and register problems, unless careful attention is paid to this issue during manufacture and use. Changes in fiber dimensions are most likely to cause problems during converting and use of paper in cases where the average orientation of fibers is not aligned with the direction of manufacture. Curl also can result if there are excessive differences in the ratio of fine particles to long fibers at the top versus bottom surfaces of the sheet, or if the drying process has resulted in uneven stresses within the sheet.

The pH Value of Paper and its Permanence. Though ordinary paper contains no liquid water, except for wet-wipe products, it is possible to evaluate paper's pH. One method involves placing a drop of distilled water on the sample and using a flat-ended glass electrode. The acidity or alkalinity of paper is determined by measuring the pH of a cold- or hot-water extract and titrating with acid or base to an endpoint (TAPPI T435 and T509, ASTM D778). The results of such analyses generally reflect the aqueous conditions under which the paper was formed. Acidic conditions have been found to accelerate the decomposition of paper, leading to loss of strength, especially under humid, warm storage conditions. Paper's folding endurance is especially vulnerable to the effects of such aging. Whereas lignin-containing pulps tend to yellow with aging, lignin does not significantly affect paper's physical permanence. Paper products manufactured under neutral or mildly alkaline conditions can maintain their physical properties for hundreds of years, regardless of whether they were formed from high or low yield pulps. Aluminum sulfate, a widely used papermaking additive, can contribute to paper's acidic nature (see the section Process Additives for charge control). Paper also may become acidified by the absorption of atmospheric pollutants such as sulfur dioxide and nitrous oxide. To avoid such effects, archival-quality papers usually contain at least 2% calcium carbonate. Fine paper is made predominantly under alkaline conditions in order to take advantage of low cost, bright $CaCO_3$ fillers (see the section Calcium Carbonate).

2.8. Nonfibrous Components of Paper.

Classes of Chemical Additives. Papermaking additives, the functions of which is discussed in the section Chemical Additives to the Fibers Slurry, fall into several identifiable groups. They include minerals, such as calcium carbonate or clay, as well as water-soluble materials. So-called "wet-end chemical additives" are added to the fiber slurry before paper is made. Additional ingredients can be applied to paper's surface at a size press (see the section Size Press and Surface Sizing). Mineral-based coatings, barrier coatings, and laminations also can be applied to the paper surface.

The performance of a limited number of paper products depends on chemical reactions of noncellulosic additives. Specialized paper coatings in which chemical reactions occur at the time of use are essential in photographic, thermal, and carbonless copy papers (see MICROENCAPSULATION; PHOTOGRAPHY). Strips of paper saturated with color-forming reagents permit rapid, inexpensive urinalyses (see AUTOMATED INSTRUMENTATION, CLINICAL CHEMISTRY). Phosphates or halogenated compounds are incorporated in papers to promote flame retardancy (see FLAME RETARDANTS: AN OVERVIEW).

For acceptable performance, some grades of paper should not contain certain chemical species. Papers used for electrical insulation must be free of electrolytes. Reducible sulfur compounds, ie, sulfide, elemental sulfur, and sodium thiosulfate [7772-98-7], should not be present in papers that receive metallic coatings or in antitarnish papers that are used for wrapping polished silver or steel items. Papermaking chemicals that unintentionally could come in contact with food must be approved by the U.S. Food and Drug Administration (FDA) as indirect food additives.

Analysis of Paper Relative to Its Chemical Additives. Procedures are available for detecting and quantifying various noncellulosic constituents of papers. Rosin size can be detected by the Raspail or Lieberman-Storch test; its concentration may be determined by extracting the paper with acidified alcohol and isolating the ether-soluble portion of the alcohol extract (TAPPI T408 and ASTM D549). Starch is detected by the blue color produced with application of an iodine–potassium iodide solution. The intensity of the blue, which is measured with a spectrophotometer, provides the basis for a quantitative starch determination (TAPPI T419 and ASTM D591). Kjeldahl nitrogen determinations are used to determine the wet-strength resins most commonly used in paper, eg, polyamidoamine-epicholorhydrin (PAAE), urea–formaldehyde (UF) and melamine–formaldehyde (MF) (TAPPI T418 and ASTM D982). Melamine may be determined by ultraviolet spectrophotometry (TAPPI T493 and ASTM D1597). Formaldehyde-containing wet-strength resins can be detected if a red-violet color appears after heating the paper in a solution of chromotropic and sulfuric acids.

Latexes of synthetic resins are identified by infrared (ir) spectrometry. Selective extraction with organic solvents is used to obtain purified fractions of the polymers for spectrometric identification. Polymeric films can be identified by the multiple internal reflectance ir technique.

Solvent extraction followed by gas chromatographic analysis is used to determine paraffin wax, antioxidants, ie, butylated hydroxyanisole and butylated hydroxytoluene, and other volatile materials. Trace amounts of chlorinated organic compounds, eg, polychlorinated biphenyls, can be determined by using a gas chromatograph with an electron-capture detector (8).

Mineral Content of Paper (Fillers and Coating Components). After fibers, the next most prevalent solid ingredients in many types of paper are fillers, especially calcium carbonate [471-34-1], kaolinite clay [1332-58-7], and titanium dioxide [13463-67-7]. Table 3 provides examples of the relative amounts of mineral, relative to other ingredients in a variety of typical paper products.

The content of mineral in and on paper can be determined by incineration (TAPPI T413 and ASTM D586). Due to loss of crystalline H_2O or CO_2 from various minerals during such analyses, ignition factors are used to calculate the original mineral content. X-ray fluorescence tests of the ash material can be used to identify the minerals and determine the ratio(s) between them. Elemental analysis by emission spectroscopy or energy-dispersive X-ray analysis can further aid in pigment identification.

Analysis of coatings is simplified if the coating can be removed from the paper in a water bath by ultrasonic cleaning. If fibers are not present, a carbohydrate determination can be used to identify gums and other carbohydrate polymers in the coating.

3. Physical Properties and Their Measurement

3.1. Directionality. Most of paper's physical properties depend on direction, ie, the machine direction (MD), cross-machine direction (CD), and thickness directions (z direction). Strength usually is greater if measured in the MD, the direction of manufacture, than in the CD. For paper made on a Fourdrinier paper machine, in which dewatering occurs only in one direction, the ratio of the two values is usually within 1.5–2.5. However both in-plane tensile quantities tend to be much larger than z-directional strength (9). This is because wood pulp fibers are long and slender, usually having length-to-thickness ratios within 20–100. The process of forming paper tends to align fibers in the plane of the sheet, with a preference for the MD. Another important factor is the tendency for paper to become stronger if it is dried under restraint, ie, prevented from shrinking during drying (see the section Drying).

3.2. Mass Per Unit Area (Basis Weight). The *basis weight* of paper, W, is the mass in g/m^2 (TAPPI T410). It also can be expressed as pounds of a ream of 500 sheets of a given size, but the sheet sizes are not the same for different paper grades. Typical sizes are 43.2 × 55.9 cm for fine papers, 61.0 × 91.4 cm for newsprint, and 63.5 × 96.5 cm for several book papers. Typical basis weights for tissue and toweling are 16–57 g/m^2; newsprint, 49 g/m^2; grocery bag, 49– 98 g/m^2; fine papers, 60–150 g/m^2; kraft linerboard, 127–439 g/m^2; and folding boxboard, 195–586 g/m^2.

3.3. Thickness (Caliper). Caliper is the apparent thickness in micrometers (μm) of a single sheet measured under specified conditions (TAPPI T411). Typical caliper values for common paper and board grades are capacitor tissue, 7.6 μm; facial tissue, 65 μm; newsprint, 85 μm; offset bond, 100 μm; linerboard, 230–640 μm; and bookcover, 770–7600 μm.

3.4. Tensile Failure Analysis. The tensile strength of paper is the force per unit width parallel to the plane of the sheet that is required to break a specimen under specified conditions (TAPPI T404). Tensile strength is often expressed as a breaking length, the maximum length that theoretically can be supported by one end without breaking. Breaking lengths for typical papers are from ~2 km for newsprint to 12 km for certain linerboard products. The values for the stronger papers compare favorably with other engineering materials. For example, breaking lengths for aluminum are ~20–25 km.

Stretch is the extension or strain resulting from the application of a tensile load applied under specified conditions (TAPPI T457). Usually the results are expressed as the maximum percentage of elongation, relative to the original length, at the moment of tensile failure. The numerical result includes the elastic and the inelastic extensibility of the paper. Stretch is generally greatest in the CD, except for creped grades. It is also common to evaluate the elongation as a continuous function of the applied load. The initial slope of the load–elongation curve defines the modulus of elasticity, E, in units of load per width.

3.5. Other Strength Analyses. Paper's bursting strength is the hydrostatic pressure required to rupture a circular area (30.5-mm diameter) when the pressure is applied at a controlled rate (TAPPI T403). Bursting strength is related to tensile strength and extensibility, and the tests are widely used throughout the industry for packaging and container grades.

Tearing strength, or the internal tearing resistance, is the average force required to tear paper under standardized conditions by which the specimen is cut prior to tearing (TAPPI T414). Internal tearing resistance should be distinguished from initial or edge-tearing resistance. Another method is based on the energy required to tear a pile of five paper sheets (TAPPI T220).

Stiffness, ie, paper's resistance to bending, is usually measured as the force required to produce a given deflection or the deflection produced by a given load when the paper specimen is supported rigidly at one end and the deflecting force is applied at the free end. Stiffness also can be evaluated by determining the resonant frequency of a cut end of a paper strip that is vibrated mechanically (TAPPI T535). The flexural rigidity of a paper sample can be defined as the product of the modulus of elasticity E and the second moment of the cross section, I. If evaluated in accordance with TAPPI T451, stiffness values are proportional to EI/W, where W is the mass per unit area. If all other factors were held constant, the stiffness of paper would be expected to vary with the cube of the thickness and directly with the modulus of elasticity. In practice, due to paper's uneven surface, an exponent <3 usually governs the relation between stiffness and caliper. Folding endurance refers to the number of folds a paper can withstand before failure under a specified, constant tensile load (TAPPI T423).

3.6. Analysis of Moisture and Resistance to Fluids.

Moisture content is determined by drying the sample at 100–105°C, until no change in mass is observed (TAPPI T412). Unless otherwise specified, the difference in mass before and after drying is expressed as a percentage of the original mass.

Internal sizing refers to the ability of a dry base-paper sheet (before any surface sizing or coating is applied) to resist passage of liquid water or other test fluid. Sizing tests often simulate end-use conditions. The Hercules size test (HST) measures the time required for colored liquid to penetrate far enough to reduce the reflectivity of the opposite side of the paper by a given amount, usually 20%. The HST data are commonly used to estimate the penetration of water at a size press, which, if excessive, can lead to the paper web breaking and poor production efficiency of the paper machine (10). The Cobb test measures how much water is absorbed by paper from one side in one minute. For prediction of the rates of penetration of various liquids into paper under dynamic conditions, such as experienced in printing, gluing, or coating, a Bristow wheel test is often employed (10).

Two common gravimetric methods are available for evaluating specific permeability of the paper to water vapor (TAPPI T448 and T464). The tests differ with respect to the temperature, as well as the vapor pressure difference that causes permeation. Permeability usually is reported in grams of vapor passing through 1 m^2 of paper per 24 h. Because of the high affinity of cellulose for water and water vapor, water-vapor permeability generally does not correlate with permeability to other vapors and gases.

3.7. Analysis of Paper's Appearance.

The most commonly measured optical properties of paper are brightness, color, opacity, and gloss. Brightness is the reflectivity of a sheet of paper for blue light having a 457-nm mean wavelength. Test equipment is designed to measure brightness either with a 45° angle between incident and measured light beams (TAPPI T452) or with a white-coated integrating sphere to produce uniformly diffuse illumination of the sample (TAPPI T525). The reflectivity is defined as the reflectance for an infinitely thick sample. Color is measured by evaluating the spectral reflectivity over the visible range of wavelengths (TAPPI T442). Opacity relates to that property of a sheet that prevents dark objects or print images in contact with the back of the sheet from being seen. It usually is evaluated by contrast ratio, which is the ratio of the diffuse reflectance of the sheet when backed by a black body to that of the sheet when backed by a white body of given absolute reflectance value (TAPPI T425). Gloss is the ability of the surface to reflect light specularly. There are numerous definitions of gloss as it relates to appearance criteria for paper, eg, specular gloss (TAPPI T480) and low angle gloss, which often is used as a smoothness test for linerboard (TAPPI Useful Method 558).

4. Manufacturing: Preparing Fibers for Papermaking

4.1. Stock Preparation.

Fibers obtained from pulping operations usually require further mechanical and chemical treatments before they can be formed into paper that meets customer requirements. The term "stock preparation" is often used for such operations (11). During stock preparation, fibers are most conveniently handled as aqueous suspensions, which can be easily conveyed, measured, subjected to desired mechanical treatments, and mixed with nonfibrous additives before being delivered to the paper machine. In integrated pulp and paper production facilities, fibers are delivered to the paper mill in slurry form. By contrast, purchased pulps and waste paper supplies usually are received as dry sheets (laps) that must be repulped (slushed) before use. The objectives of repulping are to separate the fibers and disperse them in water with a minimum of mechanical work so as not to alter the fiber properties. Repulping is accomplished in several types of apparatus, eg, the Hydrapulper (Fig. 3).

4.2. Beating and Refining. The majority of papermaking pulps obtained by chemical pulping (see the section Chemical Pulps) are subjected to mechanical treatments known as refining or beating before being formed into paper. Such treatments can improve the strength of the finished sheet. During refining the cellulose fibers are swollen, internally delaminated, fibrillated, and sometimes reduced in length. In most cases it is desirable to employ conditions that emphasize internal delamination and fibrillation. Refining tends to increase the wet specific surface area of pulp fibers, the swollen specific volume, and fiber flexibility. This flexibility allows the fibers to adopt ribbon-like shapes, thereby increasing the relative area of molecular contact (bonded area) between them in the resulting paper. Capillary forces during drying, as well as pressing operations (see the section Sheet Pressing), also contribute to the development of molecular contact between fibers.

Paper formed from unrefined kraft pulp tends to have a low apparent density and to be rather soft and weak. If the same pulp is well beaten, the resultant paper tends to be denser, harder, and stronger. If taken to the extreme, beating produces brittle, translucent, glassine-type sheets. Optical micrographs of a softwood kraft pulp before and after several periods of extensive beating are given in Fig. 4. In Fig. 5, the tensile strength, bursting strength, and tearing resistance are shown as functions of beating time for a softwood kraft pulp. It generally is true that, within the commercial range, refining increases tensile strength, bursting strength, folding endurance, and sheet density, whereas it reduces tearing resistance.

The essential operations within a modern refiner can be illustrated by considering two early methods. The first method, which usually employed mechanical energy from a water wheel, involved repeated hammer-like blows against a slurry of fibers within a vat. This manner of refining helps to explain why the term "beating" is still widely used when referring to the mechanical treatment of pulp fibers. The repeated blows, causing momentary compression, were apparently effective in producing the needed internal fibrillation of pulp fibers. However, such beaters were not well suited to regions such as Holland, where waterpower was scarce. The jerky motion of a hammer-mill was poorly suited to the operation of windmills. To address this problem, the so-called hollander beater was developed in $\sim$1690. A hollander beater consists of an elongated tub with a central dividing partition (midfeather) extending along the major axis to within a few meters of each end. A cylindrical beater roll is mounted on one side, and rectangular, blunt-tipped blades (bars) are placed around the circumference parallel to the roll axis. The roll is mounted over a bedplate, which also contains a set of rectangular bars. Circulating stock passes between the rotating roll and the bedplate. The intensity of refining is controlled by adjusting the load of one against the other. Most modifications of the original hollander represent attempts to increase capacity, improve stock circulation, and save power.

The first successful continuous refiner, the Jordan, was developed in ∼1860. The Jordan has a stationary conical shell and a conical rotating plug that fits inside the shell. Both facing surfaces have patterns of rectangular bars. The pressure between the two surfaces can be adjusted. The pulp slurry is fed into the small end of the Jordan refiner and is discharged at the large end. Other conical refiners include the Hydrafiner, which has a short, low taper, high speed rotor, and wide bars (12). The Claflin refiner has a very short, high taper plug. Vanes that fit on the wide end of the plug draw the stock through the unit (13).

Though various types of conical refiners continue to be used and developed, the majority of modern refining equipment involves versions of the disk refiner. Such equipment includes one or two rotary disks and two or four working surfaces. The surfaces are pressed together uniformly by hydraulic pressure, guided by high precision, heavy-duty bearings. Stock usually is fed through the center of one plate and leaves between the plates at their circumferences. The plates of a disk-type refiner can be relatively easy to install, remove, and store, compared to earlier designs. By having a variety of available plates, a papermaker is able to carry out needed repairs and sharpening.

A considerable range in the properties of refined stock may be realized through control of the refiner's operating variables. For example, high stock consistency, dull beater or refiner bars, low pressure, or excessively wide separation between the two sets of bars may yield a mild refining action, resulting in accentuated fibrillation and swelling. Low stock consistency, sharp bars, and high pressure between elements can result in severe fiber length reduction, with subsequent negative effects on strength. In the case of disk refiners, the user can change the size, number and pattern of rectangular bars on the opposing plates to adjust the intensity of refining action. Once the pattern, pulp solids, flow rates, and pressure settings of the refiner have been selected, a common control strategy involves maintaining a constant energy input per unit mass of pulp, on a dry solids basis. The success of this type of strategy depends on having a relatively uniform incoming stream of pulp, especially in terms of the pulp's yield (see the section Summery of Fiber Composition and Physical Attributes). Also, it is important to control the filterable solids content (or consistency) of pulp entering the refiner. Some papermakers employ a more proactive control strategy involving online measurements related to pulp freeness (TAPPI T227). The freeness data are used to adjust the energy input or pressure settings.

4.3. Blending and Metering of Paper Stock.

Many paper products contain blends of two or more fiber types. Because the ratio between the amounts of longer and shorter fibers affects the product attributes, the usual practice involves control of the filterable solids content (consistency) of each incoming stream (eg, 4% solids), followed by accurate measurement of each flow rate. Blended pulp is often kept in an agitated tank (chest), or in a series of two chests. The chest or chests provide buffer capacity, in case of system upsets.

It is common for stock from the final chest, often called the machine chest, to flow through a final refining stage, sometimes called the tickle refiner. A tickle refiner can provide the papermaker with a final opportunity to shorten the fibers. Accordingly, tickle refiners typically are fitted with relatively coarse refining plate patterns that deliver a relatively harsh effect, cutting, rather than fibrillating the fibers.

The traditional way to control the mass flow of fibers entering the forming section of the paper machine involves pumping an excess of the stock up to an elevated tank called a stuff box. The stuff box is provided with baffles, so that part of the stock can flow toward the paper machine, and the excess stock flows back to the machine chest. The hydrostatic head from the stuff box makes it possible to meter the pulp flow accurately at a specialized valve. The volumetric flow usually is monitored by a magnetic flow meter. In modern systems, this flow is automatically adjusted, based on online measurements of the product's basis weight at the dry end of the paper machine.

4.4. Approach Flow, Screening, Cleaning, and Deaerating.

After passing through the stock valve and flow meter, the fiber suspension enters a large centrifugal pump, known as a fan pump. A relatively large amount of process water (called white water) is added during the pumping process. The resulting stock consistency often is in the range of 0.3–1.5%. The fibrous suspension then passes through one or more screens to remove fiber bundles and other large contaminants.

In systems producing fine paper, the screened stock usually passes through hydrocyclone cleaners capable of removing dense particulate matter, such as sand. Within a hydrocyclone the dilute fibrous slurry is forced to spin in ever-tightening circles. The resulting centrifugal acceleration causes relatively large, dense matter to move toward the outer wall of the hydrocyclone, where it is rejected with part of the flow at the tip of the cone. Accepted stock emerges from the larger end of the hydrocyclone. To minimize losses of solids, hydrocyclones are usually set up in banks of primary, secondary, and tertiary cleaners. In such a system, a good fiber that happens to be present in the reject stream of the first bank of hydrocyclones has at least two more chances to be recovered and sent toward the paper machine.

Deaeration equipment, which involves application of a moderate vacuum, is often positioned immediately after the cleaners. In this way, the intense, swirling flow of the dilute stock as it exits the hydrocyclones helps to release bubbles of air. Stock then enters a flow spreader or intake manifold, which provides a uniform flowing stream as wide as the paper machine.

4.5. Headbox.

The slurry is then discharged into a headbox. The term headbox comes from earlier designs in which the level of dilute stock in this piece of equipment provided sufficient hydrostatic head to match the speed of the jet of stock with that of the forming fabric. With increasing paper machine speeds, such designs became obsolete. To achieve higher jet speeds, as well as to keep the headbox design relatively compact, two main types of headbox have come into common use, as follows:

In the case of air-padded headboxes, the pressure within the box is regulated with air pumps, and the stock is continually agitated with rectifier rolls, rotating hollow cylinders covered with a pattern of large holes. In the case of hydraulic headboxes there is no air space; rather the pressure is completely controlled by the incoming flow rate in the stock approach system. Microturbulence is induced in the stock by such devices as tube expansions and a relatively narrow slit-like channel.

The suspension flows from either type of headbox through a narrow opening known as the slice. The jet of suspension coming from the slice lands on a moving screen (the forming fabric) or into the converging nip between a pair of such fabrics. Subsequent forming operations are described in the section Sheet Forming, Pressing, and Drying.

5. Chemical Additives to the Fiber Slurry

5.1. Fillers. In terms of the amounts used, mineral powder products, ie, fillers are often the major additive to the fiber slurry before paper is formed. Many paper products, however, contain no mineral content at all. Examples include tissue products, milk carton board, bag paper, and filter paper. In various other types of paper, the mineral content (including the content of coatings) is often within the range of 2–40 wt% of the final sheet.

Because filler particles are much smaller than the fibers used in papermaking, often ~0.5–3 μm 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 paper's opacity and brightness. The brightness, particle size, particle shape, and refractive index of fillers influence the optical properties of the finished sheet. At the same time, filler particles tend to decrease the relative bonded area between adjacent fibers, usually resulting in a lower strength of filled paper products compared to unfilled paper. Because of a relatively high surface area of fillers, often in the range 4–20 m^2/g, their use tends to increase the demand for such papermaking additives as sizing agents (see the section Internal Sizing). Another consequence of the relatively small size of filler particles is that they easily pass through the openings in the forming fabrics of conventional paper machines. Though some filler can be mechanically sieved by the fibers themselves during the formation of paper, most papermakers rely on coagulating chemicals and high mass flocculating polymers to retain fillers onto cellulosic surfaces before the sheet is formed (see the section Retention Aids). Most commercial fillers are essentially insoluble in water under the conditions of use.

Calcium Carbonate. Calcium carbonate [471-34-1] has emerged as the most important papermaking filler. The major forms of filler-grade $CaCO_3$ are precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC). The latter category includes ground limestone and ground chalk, depending on the type of mineral deposit. Whereas limestone is obtained from hard, metamorphic mineral deposits, chalk consists of the shells of microscopic marine organisms deposited in lagoons in ancient seas. The relative ease with which chalk particles can be separated from one another, as well as the relative size uniformity of those particles, helps to explain why calcium carbonate use as a filler arose relatively early in Europe, where high quality chalk deposits are available. By contrast, in the United States it was not until the development of modern PCC technology that $CaCO_3$ became widely used as a filler in grades other than cigarette paper, where is helps to control the rate of burning. Within approximately two decades, starting in ~1980, PCC went from being a niche filler product to becoming the dominant filler in the U.S. market.

The process most often used for the preparation of PCC products can be described by the following three equations. These equations also can serve to define three key terms, calcining, slaking, and carbonation:

$$CaCO_3 + \text{heat} \rightarrow CaO(\text{burnt lime}) + CO_2 \uparrow (\text{calcining}) \qquad (1)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \ (\text{slaking}) \qquad (2)$$

$$Ca(OH)_2 + CO_2(g) \rightarrow CaCO_3 + H_2O \ (\text{carbonation}) \qquad (3)$$

Driving forces that help to explain the rapid growth of PCC use include the costs of shipping filler products, costs associated with achieving opacity targets, and the ability to control both the particle size and shape of the filler product. Substantial savings in shipping costs can be achieved in cases where the calcination step (eq. 1) is carried out near to the limestone quarry, while the slaking and carbonation steps (eqs. 2 and 3) are carried out adjacent to the paper production facility at a so-called satellite plant. That is because the mass of the CaO (lime) produced by calcination is only 56% of the mass of $CaCO_3$. By contrast, filler products such as kaolin clay require a freight charge corresponding to 100% of the mass of filler added to the paper. The reagents required at the PCC satellite plant are just H_2O and CO_2, the latter of which is often collected from smokestack gasses at the paper mill.

The cost advantage of PCC, with respect to opacity, can be understood by considering two of the filler products that PCC has tended to displace. As will be described later in this section, titanium dioxide is especially effective for achieving opacity goals, but it is much more expensive to produce than PCC.

Kaolin clay, the other major filler material, is relatively inexpensive, but it tends to be inferior to PCC in terms of brightness and opacity. By replacing the clay with PCC, many papermakers were able to achieve their opacity goals without having to use TiO_2. The shape of PCC particles can be controlled over a wide range by adjustment of process conditions during the precipitation reaction. Particles having a rosette shape (scalenohedral calcite) are favored in paper grades requiring opacity, brightness, and smoothness, while maintaining a relatively low apparent density as the filler level is increased. Other PCC shapes are favored in cases where relatively dense paper is required.

Ground $CaCO_3$ particles can be used in many of the same applications as PCC. To compensate for generally lower light scattering ability, compared to PCC, higher filler content may be needed to achieve the same optical property goals. The economic viability of such approaches can depend on the proximity of the paper mill to a GCC production source, minimizing the cost of transportation. Ground limestone products, usually specified as fine and ultrafine, can provide superior brightness, depending on the purity of the source rock. A higher energy input is required in order to grind limestone down to the desired particle size range, which is usually specified as either 60 or 90% of the particles being $<2\,\mu m$, based on sedimentation tests. Chalk $CaCO_3$ products tend to have somewhat lower brightness; they can allow somewhat higher loadings than most other fillers while maintaining a given set of physical strength specifications.

Exposure of ordinary $CaCO_3$ to aqueous solutions having pH values below ~6.5 causes the filler to dissolve. In essence, equation is forced to go toward the left. For this reason the use of conventional $CaCO_3$ fillers usually implies paper machine operating pH values of ~6.5–9. Mistaken addition of $CaCO_3$ into acidic systems, especially if aluminum sulfate is present, can result in foam problems. As will be discussed in the section Alkaline Sizes, new hydrophobic sizing agents had to be developed, suitable for use under weakly alkaline papermaking conditions, before $CaCO_3$ became widely used as a filler.

Kaolin Clay. Kaolin [1332-58-7], which is also known as China clay, is the second most widely used filler material, after $CaCO_3$. Clay is a low cost, naturally occurring, hydrated aluminum silicate having a platy shape. The generalized formula is $(Al_2(OH)_4(Si_2O_5))_2$. Kaolin occurs as natural hexagonal plates with diameter/thickness ratios of ~10:1. Variations in the specific makeup of the clays influence rheological, surface, chemical, and optical properties. Minor amounts of impurity minerals can adversely affect pigment properties (see CLAYS, SURVEY).

Clay is especially used as a filler when there are various reasons use acidic papermaking conditions. Clay products are especially advantageous in certain highly filled, supercalendered grades of paper, which achieve a glossy appearance even without the application of a coating to the paper surface.

Titanium Dioxide. Titanium dioxide [13463-67-7] is a high refractive index material, which makes it especially effective for the scattering of light. Two crystalline forms of titanium dioxide are used as fillers, anatase and rutile. In each case, the particles are generally blocky or spheroidal, having diameters of ~0.3 µm. The small size of typical TiO_2 particles, compared to most other fillers, tends to make these products somewhat more difficult to retain during the sheet-forming process.

Tabulation of Filler Attributes. Some properties of important fillers are summarized in Table 4.

5.2. Internal Sizing. Many applications of paper products require resistance to wetting or absorption of water or other liquids. For example, paper cups may require a high resistance to penetration by hot coffee. Printing papers may require some resistance to the wicking and feathering of ink-jet fluids. Butcher-wrap, juice cartons, and cartons for frozen chickens represent some of the more challenging paper and paperboard products, in terms of liquid resistance. Internal sizing can be defined as the process of adding materials to the fiber slurry to render the resulting paper more resistant to penetration by liquids, particularly water. Unsized or "waterleaf" paper freely absorbs liquids. For example, blotting paper and facial tissue usually are unsized.

If one considers only its typical chemical and structural composition, paper might seem to be a poor candidate for the job of resisting or containing liquids. Cellulose and hemicellulose molecules, which make up the majority of the fiber mass in most paper products, can generally be considered as water-loving. Although many of the hydroxyl groups in these two classes of polysaccharides will be tied up in intra-molecular hydrogen bonding, many of those groups will be available at the surface of fibers for interaction with water. Paper also is highly porous, such that the base-sheet cannot provide a watertight barrier. This leaves the papermaker with the options of either chemically treating the solid surfaces to render them nonwettable (internal sizing), adding water-repellent substances to film-forming materials added to the surface of paper (surface sizing with hydrophobic additives), or application of a plastic laminate or hot wax. In some cases, eg, beverage containers, two or more of these approaches may be applied simultaneously.

Several requirements need to be fulfilled simultaneously for a chemical substance to be effective as an internal sizing agent. The substance must have some water-hating character, which is most often provided by hydrocarbon chains or rings consisting of the equivalent of $\sim$14–20 CH_2 groups. There needs to be an effective mechanism by which the material becomes thoroughly distributed throughout the fibrous slurry. Most sizing agents are added to the papermaking furnish as emulsions. An exception to this rule is rosin soap, which is added as a micellar solution. After mixing with the fiber slurry, there needs to be a mechanism by which the sizing material is efficiently retained onto the solid surfaces, rather than just getting lost from the process with excess process water at a wastewater treatment operation. Rosin soap size is usually precipitated onto fibers and other solids by the addition of aluminum sulfate (alum). Emulsion-type sizing agents are most often stabilized with cationic polyelectrolytes, such as cationic starch. The resulting positive charge helps the droplets or particles of sizing agent to adhere onto the predominantly negative surfaces of cellulosic materials as the paper is being formed. Another requirement is that the sizing molecules need to become oriented at the solid surfaces such that they present a water-hating portion of the molecule that faces outward. The sizing molecules also need to become fixed to the surface, still in their proper orientation. In the case of rosin size product, to be discussed, the fixation most often involves aluminum sulfate, though other fixatives such as ferric chloride also can be used. Certain other sizing agents, to be discussed in the section Alkaline Sizes, undergo chemical reactions during the drying of paper, which have the potential to form covalent bonds to anchor the hydrophobic groups at the surface in a favorable orientation.

Hydrophobic character also can be developed by adding relatively high levels of emulsified wax. The reason for the lower efficiency of paraffin waxes, compared to conventional sizing agents for paper, can be traced to their lack chemical groups capable of anchoring the molecules at the solid surfaces within a paper product. Instead of forming a monolayer or submonolayer of hydrophobic groups, waxy substances are more likely to be present as beads, lenses, or as relatively thick layers.

Rosin Soap Size. Historically, the first major successes in internal sizing were achieved with wood rosin [8050-09-7]. Rosin-derived products continue to be used in a wide variety of paper grades. The major source of rosin is tall oil, a distillate collected during the preparation of kraft pulp from softwood species (see the section Alkaline Sizes). After fractionation of rosin from the crude tall oil, it exists as a mixture of terpene-type, resinous compounds. Two major components of typical unmodified rosin are the resin-acids abietic acid and levopimeric acid, each of which has a partially unsaturated hydrocarbon structure with three six-membered rings joined at the edges. The physical attributes of rosin are illuminated by one of its most well-recognized applications, the "rosining of the bow" by players of violins and related instruments. Though rosin is a solid at room temperature, it is slightly tacky and resists sliding of surfaces to which it is applied.

Most of the rosin used in the manufacture of paper is first modified by reaction with either maleic anhydride [108-31-6] or fumaric acid [110-17-8]. This Diels-Alder reaction, followed by opening of the anhydride function with addition of water, converts the abietic acid and related compounds to corresponding species that have three, rather than just one carboxylic acid group. The resulting products are known as fortified rosin size. In comparison with unmodified rosin, products containing significant amounts of fortified rosin tend to be more storage-stable, easier to emulsify, and more reactive with aluminum compounds. Before it is used, the rosin needs to be formulated so that it can easily be added to a paper machine furnish. A variety of forms of rosin products, including rosin paste and dry rosin, have been used for many years within the paper industry. Currently the most widely used rosin products fall into one of two major classes, the so-called rosin soap sizes and rosin emulsion sizes.

Rosin soap size formulations are prepared by saponification of partially fortified rosin by addition of NaOH, converting most of the carboxyl groups into their charged, carboxylate form. The majority of soap-type rosin products in current use are delivered as clear, amber-colored liquids. As the name soap implies, dilution of these rosin soap products in water, followed by agitation, creates a sudsy mixture in which the organic molecules are present mainly in the form of micelles.

Rosin products are almost always used in combination with soluble aluminum compounds, especially aluminum sulfate [17927-65-0], which is often called papermaker's alum. The order of addition, relative to alum, can make a significant difference with respect to rosin's performance. When using soap sizes, the traditional practice calls for rosin solution to be added first to the papermaking stock at a level of $\sim$0.2–2.0% solids, based on the on dry fiber. The alum is then added downstream, after the rosin has become well mixed with the stock. The traditional recommended ratio of rosin to alum is between 1:1 and 1:3. The upper end of this range reflects the fact that alum can simultaneously serve various roles, including neutralization of excess negative colloidal charges in the furnish, pH control, and allowing water to be released more quickly during the paper formation process. The pH value after alum addition is generally in the range 4–5. The reaction between the micellar rosin soap and the soluble aluminum ions results in precipitation of rosin abietate and related chemical species onto the fiber surfaces. This sizing reaction is completed while the stock is still in the form of an aqueous suspension. Because alum is acidic, NaOH is often used for pH control. Alternatively, it is possible to use an optimized ratio of alum and sodium aluminate, taking care that the two additives are separately added to the stirred suspension in different parts of the process.

An opposite order of addition, which is sometimes called reverse sizing, is often employed if the fresh water being used has a relatively high level of calcium hardness. Thus, addition of alum to the furnish ahead of rosin can minimize undesirable formation of calcium resinate products, which are not effective for sizing. Simultaneous addition of rosin and alum, though not usually recommended, is sometimes employed when there is a desire to operate the process at a pH value that is higher than usual for a soap rosin product.

Rosin Emulsion Size. Emulsions are the second main class of rosin size products. To form an emulsion, the rosin is heated above its melting point, then added to a hot aqueous solution in the presence of agitation. Sufficient base may be added during emulsification to saponify a minor portion of the rosin. The aqueous solution used for emulsification also must contain a suitable stabilizer. Historically, the most popular stabilizer for rosin emulsions was casein, a natural protein. The size particles in the resulting casein-stabilized emulsions were negative in charge, so they had little tendency on their own to deposit onto the negatively charged surfaces of cellulosic fibers. Thus one of the key roles of alum or polyaluminum chloride (PAC) [1327-41-9], when used in combination with emulsion-type sizes, was to improve the retention efficiency of the negative rosin particles onto the fiber surfaces. For purposes of retention, aluminum products tend to work most effectively within a pH range of $\sim$4.5–5.5. In recent times a majority of rosin emulsion products are stabilized by cationic polyelectrolytes. Such products tend to be self-retaining on untreated fiber surfaces.

Because rosin emulsion products remain in the form of particles, even after their deposition onto fiber surfaces, the curing reaction does not take place until paper is dried (see the section Paper Forming Machines). At that point, the rosin is able to migrate by vapor diffusion, as well as spreading of individual droplets and monolayers. Alum species adsorbed at the fiber surfaces are able to react with rosin under the hot, moist conditions present during drying. The resulting aluminum resinate, formed during the drying of paper, is chemically similar to the result of soap sizing with rosin and alum. However, the easier spreading of the relatively soft, volatile rosin emulsion particles, compared to the relatively hard precipitated particles of rosin soap size, tend to make the emulsion products more efficient.

Though the use of cationic emulsion products, as well as other chemical modifications of the rosin itself make it feasible to size paper at pH value up to 6.5 and slightly higher, rosin products are usually considered to be uneconomical under true alkaline papermaking pH values, eg, 7.5–9. Part of the reason for the fall-off of efficiency is that the high pH causes the rosin particles to gradually become saponified during exposure to the papermaking stock.

Alkaline Sizes. So-called reactive or alkaline sizing agents have become the most widely used sizing agents for use in the presence of calcium carbonate fillers. Such fillers tend to buffer the pH of the process water above $\sim$7–8.5, depending on the type and purity of the $CaCO_3$. The two major alkaline sizing agents are alkylketene dimer (AKD) and alkenylsuccinic anhydride (ASA). Pure AKD is waxy. By contrast, ASA can be a liquid or pasty solid at room temperature, depending on its isomeric form. In both cases, the sizing formulation is prepared by adding the active ingredient to a solution of cationic polymer, above the melting point of the size, in the presence of agitation. The stabilizing polymer is usually either cationic starch or a synthetic cationic polyelectrolyte of moderate charge density. The ASA size is noted for its relatively high reactivity, making it important to carry out the emulsification adjacent to the paper machine, immediately before addition. Essentially full cure can often be obtained as soon as the paper is dry. ASA size products are also noted for their propensity to form tacky deposits if they are mishandled or used in excessive amounts. The addition of aluminum compounds, such as polyaluminum chloride (PAC), is generally favorable to curing of ASA, and also helpful in minimizing problems related to tackiness. The major uses of ASA size are in production of printing papers, especially in applications where consistent frictional properties are required. AKD size is noted for its much higher storage stability, making it possible to formulate the emulsions at a central location and ship the ready-to-use product to paper mills. Major uses of AKD size include milk carton board and other products requiring a strong or durable resistance to water.

Hydrophobic Additives for The Paper Surface. Although surface sizing occurs further along in the papermaking process (see the section Size Press and Surface Sizing), it makes sense in the context of internal sizing agents to note the widespread use of hydrophobic additives that are spread at the surface of paper, ie, surface sizing. Examples of hydrophobic agents that are added along with starch and other film-forming polymer at size presses include alkyl-substituted polyurethane, styrene maleic anhydride, and styrene acrylic acid. The latter two products are often recommended for applications requiring good adhesion of xerographic toner particles.

5.3. Colorants. With the exception of some packaging and beverage grades, most paper and paperboard products made from bleached kraft fibers are prepared with colorants. Even paper products that have a generally white appearance contain small amounts of red, blue, and yellow dyes to control the tint. The major portion of dyes usually is added to the fiber suspension, although color is sometimes corrected at the size press or by applying a dye solution during calendering. Some grades, such as file folder, may be surface tinted at the size press alone. Water-soluble synthetic organic dyestuffs are the principal paper-coloring materials. Some coloring is by water-insoluble pigments, eg, carbon black. The properties of four main classes of dyestuffs are summarized in Table 5. Within each group there are wide variations from the listed generalizations.

As indicated in Table 5, pulp characteristics can play a major role in the performance of different colorants. Fiber processing also can have an impact on the resulting shade. The undyed color of the pulp affects the final color. The varying affinities between different dyes and different types of fibers and fine materials necessitate continual adjustment of dyeing parameters. Generally, increased refining deepens the shade from a given application of a water-soluble dye but does not change the amount of dye that is retained. Fillers generally scatter light more effectively than fibers, and their affinity towards a given dyestuff is likely to differ from that of the fibers; such differences can lead to a two-sided appearance of paper that is formed on a machine in which dewatering occurs mainly in one direction. The two-sided nature of paper can be made worse by the effects of dewatering devices that tend to wash fine particles away from the side of the paper that faces the forming fabric (see the section The Modern Fourdrinier Former).

In addition to the colored dyestuffs shown in Table 5, papermakers often employ fluorescent whitening agents (FWAs or optical brighteners) during production of white papers, especially those used in photocopiers. Though similar in chemistry to certain anionic dyes having a yellow hue, the spectral characteristics are markedly different. The FWAs function by absorbing ultraviolet light and reemitting light in the blue region of the visible spectrum. Major interferences to FWA effectiveness include the lignin in high yield fibers, titanium dioxide, and cationic polymers having a high charge density.

5.4. Dry-Strength Additives. Various water-loving polyelectrolytes can be used to supplement cellulosic fibers' inherent tendency to bond to each other when paper is dried. Dry-strength additives may be derived either from natural products, such as starch, or they may be petrochemical in origin. A common feature is that the macromolecule should have a high hydrogen bonding tendency, usually related to the presence of numerous hydroxyl or amide groups. As a general rule, the molecular mass of dry-strength additives is within ~10,000–2 million g/mol. Contrary to popular conception, dry-strength chemicals added to the fiber slurry generally do not fill in a substantial amount of the void area between adjacent fibers within paper. Rather, they have been found to strengthen the bonding in those areas that already would have been in contact, based on optical tests (14).

Cationic Starch. The most widely used dry-strength chemical for addition to the fiber slurry is cationic starch. The base starch may be derived from corn, potato, tapioca, as well as certain other starchy grains and vegetables. To prepare the derivatized product, the base starch is suspended as an aqueous slurry and then reacted with trimethylammonium-epoxypropane, or a similar reagent. The reaction, as described, results in quaternary ammonium groups, which provide a cationic charge that does not depend on pH. The extent of reaction is usually within the range of ~0.2–0.4% substitution, based on glucose subunits within the starch.

Ordinary cationic starch products must be cooked immediately before use. Both batch cooking and continuous (jet cooking) processes are in common use. Batch cooking usually involves ~20 min of heating the agitated starch suspension within the temperature range of ~90–95°C. Jet cooking usually involves heating the starch suspension above 120°C under pressure with steam addition, with a retention time of ~3 min at the high temperature. The addition rate of cationic starch to the fiber slurry is usually within the range of zero to ~1.5% of paper's dry mass. The upper limit of effective use of cationic starch can depend on the surface area of the wetted fibers and other solid materials in the suspension. The positive charge of cationic starch aids in its adsorption onto predominantly negative surfaces of wood-derived materials.

Other Natural Product-Based Dry-Strength Additives. Uncooked starch, when used as a dry-strength additive, can be added either to the fiber slurry or sprayed as a suspension onto the wet web of paper as it is being formed. The starch granules reach their gelatinization temperature of ~60–80°C as the paper is dried, allowing them to soften and contribute to bonding. Amphoteric starch products, which are used in the same way as cationic starch, contain phosphate groups, in addition to the quaternary amine groups. Recently, anionic starch products have been promoted as dry-strength additives for addition at the wet end of the paper machine; it is necessary in such cases to precede or follow the anionic starch addition with a cationic polymer in order to achieve effective retention of the starch on cellulosic surfaces.

Other natural products, guar gum [9000-30-0] derivatives in particular, also can be used in a similar role as cationic starch. Their relatively high molecular mass, linear character, and high solubility can give guar-based additives a strength advantage over starch products at a given level of addition. Carboxymethylcellulose (CMC) [9004-32-4] is often added in sequence with a cationic additive, such as alum or a synthetic cationic polymer, to achieve relatively high levels of dry strength.

Synthetic Dry-Strength Additives for Wet-End Addition. Acrylamide-based products are an obvious choice for use as dry-strength additives, due to their high solubility and hydrogen bonding ability. Anionic copolymers of acrylamide are usually added in sequence with aluminum sulfate or highly charged cationic synthetic polymers. Cationic and amphoteric (containing both positive and negative groups) acrylamide-based products are also used. Though the synthetic products are ordinarily more expensive than cationic starch, they often produce a greater strengthening effect, and they contribute less to biological oxygen demand of the system. Strength additives related to polyvinylalcohol, polyvinylamines, and latex also have been used.

5.5. Wet-Strength Additives. There are numerous applications in which it may be advantageous to maintain paper's integrity, as well as a substantial fraction of its initial strength, even if the product becomes completely wetted. This requirement is especially important in the case of paper towels, disposable garments, as well as paper bags, which may be exposed to rain, condensate, or spilled liquids. Though the strength of ordinary paper can be protected by the use of sizing agents (see the section Internal Sizing) or extruded plastic lamination (the section 7.3.2.), such approaches are effective only so long as the product remains dry. Otherwise, water molecules can diffuse into bonded areas and occupy possible sites of hydrogen bonding between the adjacent fibers.

Permanent Wet-Strength Resins. The term "permanent" is used to describe wet-strength additives that can maintain at least 10–20% of paper's original strength, even if the product is soaked for an extended period. The most widely used class of such additives, the polyamidoamine-epichlorohydrin resins, have maximum effectiveness when used under weakly alkaline papermaking conditions. These cationic, water-soluble polyelectrolytes have reactive azetidinium groups, which crosslink the resin when the paper is dried. The efficiency of azetidinium-containing wet-strength resins is sometimes improved by sequential addition with CMC (see the section Other Natural Product-Based Dry-Strength additives).

Other widely used wet-strength additives include melamine–formaldehyde (MF) [1017-56-7] and UF [9011-05-6] resins (see AMINO RESINS AND PLASTICS), both of which tend to be optimized under acidic papermaking conditions. Isocyanate-based resins also are under development for paper applications. While all of the above-mentioned additives are known to be reactive, capable of forming covalent bonds, it is worth noting that certain nonreactive products, such as polyethylenimine (PEI) [9002-98-6] may contribute significant wet strength to paper products.

Temporary Wet-Strength Resins. The term "temporary" implies that the additive is capable of providing a substantial degree of wet strength when the product initially becomes soaked, but that the effect gradually decays during prolonged soaking. Temporary wet strength can be advantageous if the product has a high probability of being flushed by some users, as in the case of paper towels. The best-known temporary wet-strength additives are the glyoxalated acrylamide copolymers, as well as dialdehyde starch. When paper containing such additives is dried, water-reversible hemiacetal bonds are formed between the added polymers and the fiber surfaces. Significant decay of the wet-strengthening effect usually occurs within ten minutes of soaking, and most of the effect is gone after an hour of soaking. The relative ease of repulping of paper prepared with temporary wet-strength agents means that they cause fewer difficulties in the paper mill, compared to repulping of paper after a permanent wet-strength treatment.

5.6. Process Additives for Charge Control. The term process additives is often used to denote chemicals used by papermakers mainly to improve process efficiency, rather than directly affecting product attributes. Of course, many additives, such as cationic starch as just discussed, can have multiple functions, affecting both the functional properties of paper, eg, strength, while also affecting such process parameters as retention efficiency.

Cellulosic fibers generally have a net negative surface charge, especially if they have been freshly produced by either mechanical pulping or such chemical processes as kraft pulping. This negative surface charge is a consequence of acidic groups on various ingredients of pulp fibers, including fatty acids, resin acids, hemicellulose, and various lignin-related chemical species. Because some of these charged species typically are present as colloidal particles or dissolved polymers in the paper machine systems, the net colloidal charge tends to be negative. Papermakers often have observed positive effects on such parameters as dewatering rates and the retention of fine particles during paper formation, following treatment of the fibrous suspension with enough of a positively charged additive to partly or completely neutralize the colloidal charge.

Aluminum sulfate, which also is used in the sizing of paper with rosin (see the section Internal Sizing), has been used by papermakers for many years as a charge-control agent. Alum's maximum effectiveness, in terms of such parameters as dewatering rates, generally occurs within a pH window between ∼4 and 5. The effectiveness of alum in this pH range, including its ability to neutralize excess negative colloidal charges, is attributable to the existence of oligomeric, highly positive ions. In the case of systems operating at somewhat higher pH values, papermakers can use polyaluminum chloride (PAC), which is better able to retain its positive charge and coagulating ability with increasing pH.

Highly cationic synthetic polymers, including polyamines, PEI [9002-98-6], and polydiallyldimethylammonium chloride (DADMAC) [26062-79-3] can play a similar role as alum. Papermakers can use such additives even under neutral and alkaline papermaking conditions, especially in systems using sizing agents other than rosin products. One of the functions of highly charged additives to the paper furnish can be to enhance the performance of retention aids, which will be discussed next.

5.7. Retention Aids. The term retention aids is commonly used for water-soluble acrylamide-based copolymers that have average molecular masses within the range of ∼4–20 million g/mol. The molar percentage of charged monomeric groups is usually between ~2 and 10% in the case of cationic retention aids. Anionic acrylamide-based retention aids [62649-23-4] often have up to 30% of acidic monomeric groups, though a wide range of charge density products are available. The very high chain length of retention aid macromolecules makes these additives very effective in forming bridges between adjacent solid surfaces in suspensions exposed to flow. For instance, fine particles may become agglomerated or attached to fiber surfaces. The strength of the attachments can be roughly a factor of 10 stronger than what can be achieved merely by adjusting the electrical charges of the solid surfaces in a papermaking furnish. Retention aid addition rates usually need to be optimized to achieve a balance between retention efficiency of the fine particles, the cost of the additives, and a tendency for retention aids to hurt the uniformity of paper, especially when excessive amounts are used. Retention aid polymers are commonly delivered to a paper mill as concentrated water-in-oil emulsions, other types of suspensions, or as granular powders. The concentrated material usually is diluted ~1h before use under specified conditions of agitation, followed by sieving to remove any undissolved matter.

As an alternative to acrylamide-based retention aids, it is also possible to use very high mass polyethylene oxide (PEO) [25322-68-3] macromolecules. Because these water-soluble polymers are uncharged, their use is relatively unaffected by the presence of negatively charged colloidal matter or high salt levels. However, in order to be effective, the papermaking system must also contain at least one substance acting as a “cofactor”. Such cofactors can include various phenolic resins, which appear to mediate the interaction of PEO products with fiber surfaces. Lignin, as present in high yield pulps and medium yield unbleached kraft pulp, is known to have some activity as a cofactor.

5.8. Microparticles. The term “microparticles”, in the context of papermaking, refers to such products as colloidal silica [7631-86-9] and sodium montmorillonite (bentonite) [1318-93-0]. Such microparticles, when used, usually are added as dilute colloidal suspensions to the fiber slurry either just before or after addition of a cationic retention aid, as described above. The interaction between the adsorbed retention aid polymers and the tiny particles often results in an increased rate of water release from the paper as it is being formed. Colloidal silica microparticles are sometimes called nanoparticles, since the primary particles are often in the range of 2–5 nm. Superior effects, in terms of increased retention efficiency, have been observed in the case of some colloidal silica products in which the primary particles are fused together as short chains. Sodium montmorillonite particles are obtained from natural deposits of a so-called “swelling clay”. Under proper ionic conditions and shear, the montmorillonite exfoliates into platelets as thin as several nanometers.

5.9. Defoamers. Entrained air and visible bubbles in papermaking stock can cause operational problems. For example, tiny entrained air bubbles can decrease the rate of water release from paper, sometimes making it necessary to slow down the machine. Visible bubbles can cause blemishes on the paper surface. Foam in tanks can aggravate deposit problems. Substantial losses of solids may occur if foam builds up and pours onto the factory floor, from which it is usually discarded to a wastewater treatment facility. Most foam problems in paper mills result from excessive concentrations of surface-active materials in the process water. Foam can be especially problematic if polyelectrolytes, such as wet-strength agents or starch products, are added at levels beyond what can adsorb onto fibers and other solids in the suspension.

In addition to the deaeration equipment already mentioned, papermakers employ formulated mixtures known as defoamers or antifoams to inhibit or break foam bubbles. The most essential ingredient of a typical defoaming agent is a water-insoluble surfactant. Many defoamer formulations also contain hydrophobic particles, which may be comprised of hydrophobic silica or ethylenebis(stearamid).

6. Sheet Forming, Pressing, and Drying

6.1. Paper Forming Machines. Continuous sheet forming and drying came into use in ~1800. Two basic designs that enjoyed early popularity were the cylinder or vat former, and the Fourdrinier former. Cylinder machines employ a wire-covered cylinder, which is mounted in a vat containing the fiber slurry. As the cylinder revolves, water drains inward through the screen, and the paper web is formed on the outside. The wet web is removed at the top of the cylinder, passes through press rolls for water removal, and then passes around rotating, steam-heated cylinders. By contrast, a Fourdrinier machine uses a long, continuous fabric screen supported by various devices that improve drainage. The fiber slurry, which is introduced at one end as a jet, coming out of a pressurized headbox, loses water as it progresses along with the continuously moving fabric screen, thereby forming the sheet. A Fourdrinier paper machine is shown diagrammatically in Fig. 6.

Paper machines have undergone extensive mechanical developments since the 1950s, although the principles employed have changed little. In modern cylinder machines, the simple vat construction may be replaced by systems in which the fiber slurry flows either concurrent or countercurrent with the motion of the cylinder; such modifications can help achieve a more optimum average alignment of fibers for different paperboard applications. In other cases, cylinders are fitted with headboxes.

The Modern Fourdrinier Former. Fourdriniers remain common in the industry for a very wide variety of paper and paperboard. The web produced can vary from 1 to 10 m in width and, when one includes the press and dryer sections, the machine may be >200 m long. On a modern Fourdrinier device the forming fabric screen is supported by hydrofoils (foils) and suction boxes. As shown in Fig. 7, foils are wing-shaped elements that induce a vacuum, helping to draw water from the wet web of paper. The intensity of the dewatering effect can be adjusted by changing the design, the angle of orientation relative to the fabric, and the spacing between adjacent foils. After passing over the initial foils, the fabric and sheet pass over suction boxes, with gradually increasing vacuum, where more water is removed. Most paper machines also include a suction couch roll, where relatively high vacuum is applied for additional water removal before the paper web enters the press and dryer sections of the machine.

The maximum production speed of a Fourdrinier machine usually is limited either by the dewatering capability of the forming section or by the evaporation rate in the dryers (see later). In relative terms, heavy paperboards require longer drying times and slower speeds. Very dense papers, eg, glassine, greaseproof papers, and condenser tissue, are difficult to dewater in the forming and press sections, and production speeds must be lower, compared to other paper products having similar weights. With the advent of the suction pickup, which closes the draw between the forming and press sections, speeds of newsprint machines increased from 400 to 800 m/min. Closing the transfer of the sheet through the entire press section and increasing the dryness at the first open draw into the dryer section from 35–38 to 41–44% combined with careful designs of the web path through the dryer section has increased newsprint machine speeds to ∼1500 m/min. It is common for Fourdrinier machines to operate at 800–1200 m/min. Drying capacity restraints and difficulties in reeling the product limit modern tissue machine speeds to 1500–2000 m/min, though most tissue machines operate at lower speeds.

Gap Formers. Though Fourdrinier paper machines and vat formers, as just described, continue to be widely used, the majority of new installations of paper forming equipment employ pairs of forming fabrics. In such machines the jet of stock is directed into a gap as the fabrics come together. Because there is no free surface between the wet web and air during the formation of the paper, twin-wire formers offer more stable high speed operation.

A related innovation has been the hybrid former, which blends features from Fourdrinier and twin-wire designs. Many large Fourdrinier wet ends have been retrofitted as hybrid machines with top wire units to achieve higher operating speeds. These retrofits have been popular for lightweight sheets, eg, tissue, towel, and newsprint, and they also have been used for fine paper grades, corrugating medium, and linerboard.

In twin-wire formers, the water mainly is drained from the fibrous slurry by pressure rather than vacuum. The two forming fabrics, with the slurry between, are wrapped around a cylinder or a set of supporting bars or foils. The tension in the outer fabric results in a pressure that is transmitted through the slurry to the supporting structure. Drainage can occur in both directions, which usually results in a more symmetrical product. An example of a twin-wire former is shown in Fig. 8.

Paperboard Machines With Multiple Formers. Boxboard, as used for packaging cigarettes, clothing, jewelry, and other small items, often consists of three to seven separate webs that are formed from different raw materials and continuously pressed together while still wet. Multiply construction can offer flexibility in fiber composition, such as the placement of bleached fibers in an outer ply and less expensive fibers in central plies. Because of the number of plies and wide variations in speed requirements, there are a large number of different designs for board-forming sections.

The forming units described in the preceding sections all receive the incoming slurry at a low consistency, typically 100–300 kg water/kg solids, and the paper web leaving the couch typically contains 4 kg water/kg solids. The water removed during paper formation is often called white water because it may contain fiber debris, mineral filler, and other fine material, giving it a milky, turbid appearance. White water is reused for dilution of the incoming stock, as well as for regulation of stock consistency. After extensive filtration, to remove solids, white water also can be used in showers on the paper machine, reducing the amount of fresh water utilized in the forming process.

6.2. Sheet Pressing. The sheet leaving the forming section may contain about five parts of water per part of fiber. The strength of the wet web at this point is mainly a consequence of capillary forces within the films of water between adjacent solid surfaces. Removal of additional water is achieved in the nips between pairs of rolls, usually with one or two carrier felts. The press rolls may be solid or perforated, and often suction is applied through the interior. As the sheet passes through each press nip, the felts act as porous receptors of water. The water content of the sheet usually can be reduced by pressing to 1.9–1.2 parts of water per part of fiber without deleteriously affecting product quality. The mechanical energy expended in pressing water from paper is several times lower in comparison with the heat energy required to evaporate the same amount of water.

In a conventional roll-type press, there usually is a limit of applied pressure, beyond which a wet web of a certain moisture and composition will become crushed, losing its integrity. Even when using a series of two to four such presses, the maximum final solids content is usually $\sim$40–50% solids, depending on the product and the equipment. Intense pressure also can force changes in the relative positions of fine particles in the web, and the layers adjacent to felts may become denser than the rest of the web. Higher solids levels before drying usually can be achieved by installing a shoe-press design in which one of the press rolls is replaced by a solid steel belt, which partly wraps the adjacent roll. In the extended nip of a shoe-press, pressure is maintained with a hydraulic fluid behind the belt, opposite to the roll. The higher residence time of the wet web in the nip allows for the passage of more water into the felts.

6.3. Drying. Most of the water remaining in the paper web after pressing has to be removed by evaporation. Due to various losses, heat energy input must exceed the theoretical amount needed to vaporize liquid water. Because drying is expensive in terms of both capital equipment and operating costs, the process often is the bottleneck of production. Most dryer sections of paper machines involve a series of steam-heated rotating cylinders. Alternate sides of the wet paper are exposed to the hot surfaces as the sheet passes around successive cylinders. In most cases, except for heavy board, the sheet is held closely against the surface of the dryers by stiff fabrics having high permeability to steam and air. Heat is transferred from the hot cylinder to the wet sheet, and water evaporates. Most dryer sections are covered with hoods for collection and handling of the air, and for preheating of incoming air. The final moisture content of the dried paper usually is 4–10 wt.% (see the section Water Content of Paper Products.).

Other types of dryers may be employed for special products or situations. For example, the Yankee dryer, consisting of a single, unusually large steam-heated cylinder, 3.7–6.1 m diameter, dries the sheet from one side only. The Yankee is used extensively for tissues, particularly where creping is accomplished as the sheet leaves the dryer. Yankee dryers are also used for making machine-glazed papers, where the intimate contact with a polished dryer surface produces a high gloss finish on the contact side. In addition to being heated from the inside, Yankee dryers often employ jets of hot air, which are directed against the sheet. Through-air dryer systems, which draw hot air through the wet, are used for certain tissue and towel products. Noncontact dryers, employing such features as ir heating, air impingement, and air-turn conveying systems are widely used in paper coating operations (see the section Pigment Coating).

7. Size Press, Coating and Converting

7.1. Size Press and Surface Sizing. The size press on a paper machine is a device where an aqueous polymeric solution can be applied to the paper's surface. The primary purpose, in most cases, is to increase surface strength. Starch solutions, the most widely used size-press additives, penetrate part way into the sheet, usually forming a discontinuous film. Such treatments tend to decrease linting, dusting, and picking in uses such as offset printing and photocopying.

It is important not to confuse the term "size press" with the terms "internal sizing" and "sizing agent". The latter terms were introduced in the section Internal Sizing in the context of using chemical additives to make paper products resist water. Though papermakers have the option of using various water-resistive additives at the size press, the application of starch to the paper surface does not, by itself, tend to resist penetration of the paper by aqueous fluids.

Underivatized starches usually have a cost advantage relative to other film-forming materials available for use at the size press, and, if used with care, the papermaker can expect to increase the paper's stiffness, pick resistance, and resistance to air penetration. To achieve suitable low viscosity levels for efficient size-press operations, the molecular mass typically is reduced, either by enzymatic treatment with α-amylase [65996-64-7] or by oxidative hydrolysis with ammonium persulfate [7727-54-0]. A 10% solids solution is typical.

Various premium starch-based products also can be used at the size press. The molecular masses of such products typically are adjusted to a desired range by the supplier during their manufacture. Products delivered in powder form generally require heating in water (see the section Cationic Starch). Some premium starch-based products can be listed roughly in order of increasing perceived quality and/or cost as follows: touch-oxidized starches; hydroxyethylated starches; and cationic starches. Hydroxyethylated starches [9005-27-0], in particular, have the potential to form tough films, relative to unmodified starches. Cationic starches have been reported to stay nearer to the paper surface, a factor that has the potential to make them more efficient for development of surface strength.

Synthetic water-soluble polymers also can be used in size-press applications. Such products usually are added either for strength enhancement or to increase the paper's resistance to fluids. Polyvinyl alcohol can be used in situations requiring high strength. Partially hydrophobic, but water-dispersable copolymers, including styrene maleic anhydride (SMA) products, styrene acrylate (SA) products, and alkyl-substituted polyurethane products, usually are added as a diluent in a mixture comprised mainly of starch. Other common size-press additives include fluorescent whitening agents (in the case of some white papers), dyes, defoamers, and biocides.

For most of the history of machine-made paper, size press equipment basically consisted of a nip between a pair of rolls. A “pond” of size-press solution was poured into the incoming nip at both sides of the paper web. Excess solution, not passing through the nip, merely drained from the two ends of the size press, later to be recirculated back to the nip. Size presses can be configured to pass the paper web through a size solution or over a roll that has been wetted with a size solution.

In new paper machines and rebuilds such conventional size presses are giving way to metering size presses. The starch, with or without hydrophobic additives, is metered to a thin film on the size press cylinders by blades or rods. The wet film is then transferred to the paper. It is also possible with modern metering size presses to apply pigmented coatings. Metering size presses can thus provide a form of inexpensive on-machine roll coating.

7.2. Pigment Coatings. Pigment coatings are compositions of minerals and binders with small amounts of additives. Such coatings are applied as high solids aqueous suspensions to one or both sides of a paper web. Main goals of coating are 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. Pigment coatings tend to be porous, because the binder adhesive is usually insufficient to fill the void spaces among the pigment particles. This porous structure is responsible for many of the desired properties of the coated papers. For example, the high opacity of the coatings results from the scattering of light from the pigment–air and binder–air interfaces. Because the particle size of coating minerals is about a factor of 10 smaller than the width of typical papermaking fibers, there is potential to create a much smoother surface, compared to uncoated paper. In many instances, titanium dioxide is used to enhance opacity. Because of the high refractive index of TiO_2, light is scattered not only at the titanium dioxide–air interface, but also at the interfaces of TiO_2 with binders and other pigments.

Pigment coatings normally are applied to the base paper in the form of water suspensions and are referred to as coating colors. The total solids content, ie, pigment plus binder, may vary widely. Blade coatings range from 50 to 70%; conventional pigmented size-press coatings vary from 6 to 15%. After application, the coating must be dried by removal of water from the film. In 1933, the first roll coater was installed as an integral part of a paper machine. These on-machine coaters produce a low cost coated paper used largely for magazines. Coating of paper off-machine at speeds greater than paper machine manufacturing speeds is possible with the use of the various available blade coaters (15).

Drying methods following coating operations include air or convection drying, contact or conduction drying, and radiant-energy drying. The speed of a coating operation often is restricted by the rate at which the water can be removed from the coating without blister formation or excessive migration of components to the hot surfaces.

Coated paper also may be supercalendered to improve surface properties, eg, smoothness and gloss. In a supercalender, the paper is passed successively through the nips of a stack of alternating hard steel and soft rolls. The pressure causes the soft roll to deform, which burnishes the surface of the sheet against the polished steel surface. This action softens the coating binder and causes greater alignment of clay platelets, yielding a glossy, level surface. The properties of the final surface are functions of the coating composition, number of rolls, pressure, temperature, and operation speed. The process also tends to densify the sheet and thus to reduce porosity.

Mineral pigments comprise 70–90% of the dry solids in paper coatings (16). In nearly all cases, the individual particles of the pigments are $<5\ \mu m$ in equivalent spherical diameter, and they average $<1\ \mu m$. Refractive index, particle size, crystal structure, light scattering and absorption, and adhesive demand are important characteristics. Minimum amounts of binders are used to hold the coating together, because the binders are more expensive than the pigments. Also, excessive amounts of binder can adversely affect the opacity and brightness of the coatings by filling in the air–pigment interfaces that scatter light. The most widely used coating minerals are fine kaolin clays and ground calcium carbonates.

In coating formulations, the proportion of binder can vary from $\sim$5 to 25%, based on the pigment. The optimum proportion depends on product objectives, as well as the strength of the binder. Traditional binders included animal glue, which was replaced in the 1800s by casein [9000-71-0], and later by soy protein. Recently, starch and latex products are the most widely used coating binders. As discussed in the context of size-press applications, coating starches must be reduced in molecular mass to lower their solution viscosity. Starch-based coatings can be made more resistant to water by the use of aldehyde-donor cross-linking agents, eg, glyoxal [107-22-2]; however, these materials increase viscosity. Exceptionally strong binders, eg, poly(vinyl alcohol) [9002-89-5], can be used in coating formulations. Although polyvinyl alcohol is expensive and highly viscous, only small amounts are required, and it is characterized by good optical properties.

Synthetic latex products have become dominant for high speed coating operations. They generally have low viscosity, which permits high solids content of the coating color. Latex-based coatings are distinguished by high gloss, good response to calendering, good ink holdout (nonblotting character), and good water resistance. The styrene–butadiene latex [9003-55-8] is commonly supplied in a 60:40 ratio of styrene to butadiene. It is used with starch in such products as publication-grade papers. Acrylic-based emulsions are used especially on paperboard. These materials are odorless, which is necessary for coatings to be used on paperboard for food packaging. The acrylics provide high gloss and good ink retention. Poly(vinyl acetate) [9003-04-7] can be used in place of acrylics if resistance to moisture and grease are needed.

Various additives are used in coating formulations to control coating behavior during application or to alter the finished product. Phosphates are widely used to disperse coating pigments, helping to improve high speed flow characteristics in the formulation. Various binders contain surfactants or polymeric stabilizers, which have to be compatible with other coating components. Lubricants, plasticizers, and flow modifiers include both soluble and insoluble soaps, sulfated oils, wax emulsions, amine products, esters, etc. Since some of the substances just mentioned can stabilize foam bubbles, coating formulations also contain defoamers (see the section Defoamers). Lubricants such as calcium stearate [1592-23-0] improve flow, coating smoothness, finish, printability, and antidusting effects. Humectants, eg, glycerol derivatives, are used in small amounts as plasticizers and aid in the development of the finish on the sheet. Materials used to increase the moisture resistance of a coating surface or to insolubilize the adhesive may react with the hydrophilic groups in the adhesive or cross-link the polymer chains to prevent swelling with water and subsequent loss of binding strength. Decreased water sensitivity can be achieved by adding urea– or melamine–formaldehyde resins, glyoxal, or ammonium zirconium carbonate with the coating formulation. Some resistance to moisture is obtained when latex is included in the coating formulation.

7.3. Barrier Coatings and Lamination. In some packaging applications it is necessary to provide a barrier against water, water vapor, oxygen, carbon dioxide, hydrogen sulfide, greases, fats and oils, odors, or miscellaneous other fluids. A satisfactory water barrier often can be achieved with sizing agents (see the section Internal Sizing). A grease or oil barrier can be provided by densifying paper made from well-beaten fiber to form a pinhole-free sheet or by coating the paper with a continuous film of a material resistant to the particular grease.

Paraffin wax [8002-74-2] and related products usually are applied in a molten form. Paraffin is low in cost, resists water vapor, and it 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 chilling. Modifiers, eg, microcrystalline wax, polyethylene, or ethylene–vinyl acetate copolymer, can improve the durability and film strength, raise the softening point, and increase the gloss and heat-seal strength of the coating. Polyethylene coatings are more durable and flexible, and thus have replaced paraffin in many applications.

Polyethylene [9002-88-4] and other barrier polymers such as ethylene–vinyl alcohol [25067-34-9] are applied by extrusion or coextrusion with intervening tie layers, producing a laminated product. Polymer pellets are heated rapidly with minimum air contact, and each molten polymer is extruded through a die and immediately laminated to the paper.

Solvent systems permit the formulation of highly sophisticated coatings, comprised of a wide variety of polymers and modifiers. Disadvantages include high solvent costs and the necessity for a solvent recovery system. The resins used include many of the same types used for coated fabrics or for industrial coatings, eg, cellulose derivatives, rubber derivatives, butadiene–styrene copolymers, vinyl copolymers, poly(vinylidene chloride), polyamides, polyesters, and alkyds. High solids content at minimum viscosity is available with emulsion or latex coatings.

7.4. Converting. The term converting includes a wide variety of operations that can follow the initial production of paper and paperboard products to make them more suitable for a variety of uses. Among the many converting operations are sheeting, embossing, impregnating, saturating, laminating, and the forming of special shapes and sizes, eg, bags, envelopes, and boxes (see PACKAGING, CONVERTING).

8. Environmental Concerns and Production Efficiency

8.1. Reducing Environmental Impacts. The papermaking process, by its nature, has potential to be environmentally friendly and sustainable. Paper is composed mainly of natural, renewable raw materials. Cellulosic fiber used in papermaking is derived from photosynthesis, which takes carbon dioxide from the atmosphere and converts it into O_2 and biomass. Most of the material in paper can be recycled, reducing the amount that gets disposed in other ways. Though relatively inexpensive, in comparison with other manufactured products, paper and paperboard can maintain most of their strength and other properties for many years. Responsible use of forestlands by the paper industry promotes tree planting and growth on lands that might otherwise be used for urban sprawl and other uses that do not take up CO_2 from the atmosphere.

Two particular environmental concerns for papermaking are energy use and the handling of liquid and solid wastes. As was noted in the discussion of the wet-pressing and drying of paper, the evaporation of water is the biggest single energy use in a typical paper mill. Fortunately, in the case of integrated pulp and paper facilities, much of that energy can come from steam generated by combustion of lignin byproducts and other organic chemicals in the spent pulping liquors. The incineration of such liquors in the kraft process results in regeneration of the pulping chemicals, in addition to providing high pressure steam to generate electricity. It can be said that the paper machine gets much of its the energy for free, since the drying operation can use relatively low pressure steam that is no longer efficient for use in generators. As discussed earlier, evaporative energy requirements can be reduced by installing extended-nip wet-presses, which can increase the solids content of the web entering the drying operation. Attention to dryer-felt tensions, condensate handling within dryer cylinders, and ventilation of the air-pockets surrounding dryer cylinders all have the potential to improve the efficiency of drying.

Year by year, less fresh water is used, on average, to produce a unit mass of paper in various production facilities (6). This trend is motivated by such factors as the cost of fresh water, limits on the concentrations or amounts of substances in discharged water, and the costs associated with wastewater treatment. Water-reduction strategies usually involve replacing fresh water with recirculated process water. Recirculation occurs at various levels within a typical paper machine. First, with few exceptions, the primary circuit of flow involves dilution of incoming fiber slurry (the thick stock) by process water that has been removed during the forming process (the white water). White water also is used for regulating the filterable solids level (consistency) of fiber slurry before such operations as refining and metering of stock flows. Also, fresh water may be replaced by strained and filtered white water in various showers, such as those used to control build-up of foam or to wash roll or fabric surfaces in the forming section of the machine.

Water recirculation has a side-benefit of generally reducing losses of fine cellulosic materials, mineral, and other colloidal material to the wastewater treatment system. The three main principles by which save-all fiber recovery systems operate are filtration, flotation, and sedimentation. If these are operated efficiently, the net loss of cellulosic materials can be <1%. Effective use of a retention aid (see the section Retention Aids) during formation or at a save-all can further reduce losses of solids from the paper machine system.

Pulp and paper mills have installed primary and secondary treatment systems to control liquid effluents (17). Primary treatment involves settling basins and/or tanks, ie, clarifiers. These remove ~85–100 wt % of solids, eg, fiber fines, mineral particles, and colloidal matter. Primary sludges, which are removed by the primary clarifiers, generally cannot be reused by the mill to make the same product (18). However, many mills use the sludges in lower grade products. Secondary wastewater treatment involves the controlled growth of bacterial sludge. Nutrients, such as nitrogen or phosphorous, may be added as needed to support growth of the microorganisms. Both aerobic and anaerobic treatment systems are used. Equipment for various biological waste treatments includes lagoons, activated sludge with air and oxygen, trickling filters, clarifiers, modified biological systems containing activated carbon, and combinations of these. Secondary treatments generally remove 90–95% of the biological oxygen demand (BOD), most solids, and most of the toxicity. Color is more difficult to remove, sometimes requiring so-called tertiary treatment steps. Sludges from secondary treatment tend to be extremely hydrophilic and are difficult to dewater.

As more process water is recycled, more nonpathogenic microbial growth, ie, slime, tends to develop in the mill system. Entrained slime can produce blemishes and holes in the paper web. Some strategies to reduce the impact of slime include treatment of the system with organic biocides, or with oxidizing agents such as chlorine dioxide or hydrogen peroxide. To reduce the toxicity associated with biocide use, progress has been achieved with certain surfactants that interfere with the buildup of biofilms on the surfaces of processing equipment. The efficiency of any form of slime control is greatly increased by appropriate mill cleaning procedures. Thus, it is common practice to periodically stop operations and clean the paper machine system with highly alkaline conditions, usually with the addition of detergents. Acidic treatments also can be used, depending on the nature of the materials that tend to deposit in a given paper machine system. More recently, enzymes have become widely used for periodic cleanings, avoiding the need for high temperatures or strong base or acid solutions.

8.2. Sludge Handling and Disposal. The two kinds of sludges generated by pulp and paper mills, primary and secondary, can differ considerably in character (19). Primary sludges mainly comprise cellulosic and mineral matter. Secondary sludges are largely biological, and they and harder to handle and dewater (20). In addition, wastes resulting from several sources within the mill can include, bark, sawdust, dirt, knots, pulpwood rejects, fly-ash, cinders, and slag.

Solids content of wet sludges can be 1–40 wt.%. The operating plan for a land-disposal site depends on the fluid state of the sludge (21). Sludges of 30–35 wt.% solids from a paper recycling or deinking operation may be in a highly fluid state, whereas a low ash, high fiber pulp mill sludge at 15–20 wt.% solids may be quite dry and stable. Sludge handling processes can include thickening, stabilization, conditioning, dewatering, and incineration. Though most sludges are landfilled, some are used in lower grade products such as landscaping bricks, or used as soil conditioners for agriculture. Some primary sludges from papermaking or coating operations have been incinerated to recover their mineral content, which has then been used for products not requiring a high brightness.

8.3. Water Quality Assessment. Starting in the mid-1970s, there has been increasing emphasis on the assessment and control of effluent water quality (21,22). Key indicators of effluent water quality are the BOD, the total suspended solids (TSS), the absorbable organic halides (AOX), chloroform content, and the water's toxicity towards various organisms. A single organism as an indicator of stream quality has been replaced by community compositional and structural analysis. Thus, total effluent effects on a broad scale can be realized. Other measured parameters are algal assays, fish surveys, sediment mapping, effluent plume mapping, sediment oxygen demand, and socioeconomic impacts.

9. Common Grades of Paper and Paperboard

It can be useful to distinguish between paper products, ie, products having basis weights below $\sim$100–150 g/m^2 versus paperboard products, which is generally thicker and stiffer.

9.1. Paper Grades. Newsprint paper usually is comprised mainly of mechanical pulps, such as thermomechanical pulp (TMP) or groundwood. The fiber portion also may contain a minor portion of bleached kraft pulp. Newsprint also can be made from deinked old newspaper (ONP), often supplemented by deinked old magazine paper (OMP) or mixed office waste (MOW). Though newsprint traditionally was not a filled grade, there is a trend toward increased use of clay or calcium carbonate, especially in publications that use colored images.

The base-stock for light-weight coated (LWC) paper is often quite similar to that of newsprint. However, the coating operation places high requirements on sheet uniformity, including the absence of holes, as well as cross-directional uniformity in weight or density. The coatings, which can comprise up to about one-half of the mass of the final product, are usually applied right on the paper machine, using blade coaters. The main uses of LWC are in magazines, as well as for advertising inserts in newspapers and direct mail.

Uncoated papers for offset lithography and xerographic printing, including use in personal printers, are usually mainly comprised of bleached kraft fibers. Precipitated calcium carbonate (PCC) is the most widely used filler in such grades, and filler levels are most often in the range 5–30%, based on dry mass. Most uncoated fine papers contain $\sim$0.5–1.5% of cationic starch that was added to the fiber slurry. Additional starch, added at a size press, is often in the range of 2–5% of product mass. The most common basis weights are within 40–100 g/m^2. Surface strength is especially important in products to be printed by offset lithography. Controlled stiffness, lack of curl tendencies, and controlled electrical conductivity are critical in papers used for xerography.

Bleached kraft pulp is also the main component of products intended for high end graphic uses, including fine rotogravure and offset images for posters, calendars, brochures, and fancy reports. A characteristic feature of such grades is that multiple layers of coatings are often applied. Both on-machine, off-machine, and combinations of coating strategies are used.

Paper for grocery bags, fast-food bags, and similar applications must have a high resistance to tearing. The fiber of choice usually is softwood kraft, which may be unbleached or bleached. To maximize the paper strength, the filler content may be low or zero. Wet-strength (see the section Permanent Wet-Strength Resins) and internal sizing treatments (see the section Internal Sizing) are sometimes used to resist rupture if the bag comes into contact with wet food, rain, etc.

Requirements of wrapping papers are very diverse, but they often involve resistance to various types of fluids. Some other wrapping papers need to be heavily treated with internal sizing agents or barrier coatings to protect various contents from aqueous fluids. Fluorochemical treatments, silicones, and laminated layers may be used to hold out aggressive fluids, such as meat juices, in the case of butcher wrap.

The term décor paper denotes the uppermost cellulosic layer of saturated laminate products used for furniture and countertops. For example, décor paper carries the imitation wood image for many furniture products that actually are made from pressed, resin-filled fiberboard. High opacity, uniformity, and a highly porous nature are key requirements of the grade. The high opacity requirements usually imply a relative high usage of titanium dioxide as a filler. A uniform and porous sheet is needed so that resins, such as melamine-formaldehyde resin can penetrate thoroughly into the sheet during a saturating operation.

Filter papers are another type of product that requires uniform and relatively high porosity. A highly porous sheet can be achieved by use of kraft fibers having a relatively low degree of refining. Because many filter papers become wet during use, it is common to employ wet-strength agents in their preparation. Filter papers also can be prepared with a wide range of non-wood fibers, including synthetics.

The everyday use of tissue paper products is in contrast to the rather complex and varied methods involved in its production. Bleached softwood kraft pulp has been a major component of tissue grades, though there is increased use of hardwood fibers (especially for softness), as well as use of recycled fibers from mixed office waste. The traditional method for preparation of tissue paper involve use of a Yankee dryer (see the section Drying). Conditions of adhesion between the web and the polished cylinder surface are optimized, mainly by chemical addition, in order to achieve a controlled degree of crepe at a doctor blade. To increase adhesion to the Yankee surface, papermakers may add starch, wet-strength resins, or polyamines. To reduce adhesion, they may use emulsified paraffin [8012-95-1], silicone oil, or polyethylene glycol (23). Alternative methods of tissue preparation include use of low wet-press conditions, through-air drying, and multiple creping. In addition, tissue products often have two or more ply construction, as well as perforations.

In addition to usually having a higher basis weight, towel grades of paper usually differ from tissue grades with respect to wet-strength requirements. Whereas many tissue paper products must be compatible with the flushing requirements of septic systems, most towel grades need sufficient wet-strength to withstand the pressures of rubbing, while in the wet state. Depending on the application, the wet-strength requirements may be met either with temporary wet-strength agents, such as glyoxylated polyacrylamide (see the section Temporary Wet-Strength Resins), or permanent wet-strength agents, such as polyaminoamide-epicholorohydrin.

9.2. Paperboard Grades. The top and bottom layers of typical corrugated boxes are ideally formed from unbleached softwood kraft fibers of intermediate yield or lignin content. An increasing proportion of linerboard products are composed partly or completely of old corrugated container (OCC) pulp. Up to ~10% content of filler can be used in some linerboard grades, especially in cases where the boxes will be used for point-of-sale advertising. There is a trend towards greater use of multiply forming, in which the top layer may be comprised of bleached fiber, often with a significant level of calcium carbonate filler. Linerboard products are pressed and calendered to relatively high density. Most linerboard products are internally sized to resist water, though it is important not to have such high resistance as to defeat the starch adhesive used in corrugating operations (see below). The most important physical attribute of linerboard is its resistance to edgewise crushing.

Corrugating medium is the type of paperboard that will be compressed into a repeating sinusoidal pattern to act as a spacer within a combined-board corrugated container. Stiffness and compression resistance are key attributes. High yield kraft of neutral sulfite semichemical pulps are preferred (see the section Mechanical Pulps with Chemical Treatment), though recycled fibers are also used. Because the resins in the high yield fibers can cause excessive development of water resistance, which can interfere with gluing of the board construction, rewetting agents are often applied at the time of manufacture.

Fine bleached board products include posterboard, file-folder, index card, and similar grades. Some of the desired properties can include brightness, uniform surface characteristics, and stiffness. Bleached kraft fibers are usually the main ingredient, and fillers are often used. Smoothness, gloss, and various printing characteristics can be improved by coatings, as already discussed.

Base-stock for paper cups, milk carbons, juice containers, and similar products is generally made from unfilled bleached kraft pulp. Key attributes include stiffness, resistance to water penetration, and compatibility with plastic laminates. Fluid resistance is generally achieved by the wet-end addition of alkylketene dimer (AKD) size, which is often added together with cationic starch, which contributes to strength. In the case of board made for aseptic packages, rosin size emulsion is often used in combination with the AKD size in order to withstand the effects of peroxide, which is used as a disinfectant. Liquid packaging board may be treated with additional starch at a size press to develop stiffness and better adhesion to an extruded plastic layer. Extruded polyethylene is used for milk cartons. Citrus juices generally require the use of multi-layered plastic laminates, having the ability to resist a variety of penetrants, including oxygen from the air, as well as water vapor.

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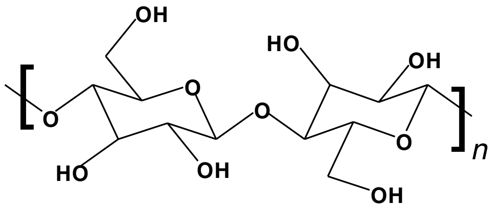

Fig. 1. Cellobiose [528-50-7], the repeating unit of cellulose.

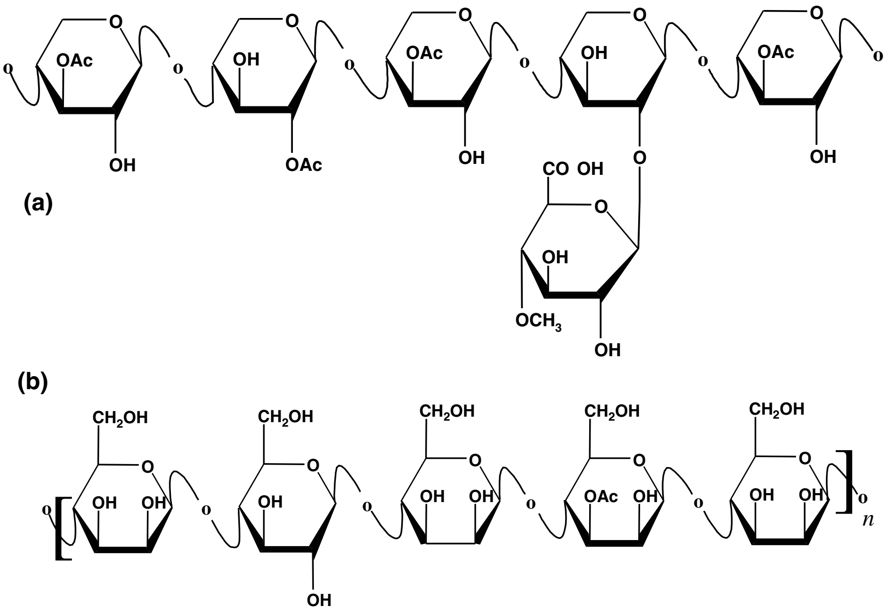

Fig. 2. Molecular structure of typical hemicellulose molecules from (**a**) hardwood, and (**b**) softwood tree species.

Fig. 3. The hydrapulper. (Courtesy of Black Clawson Co.).

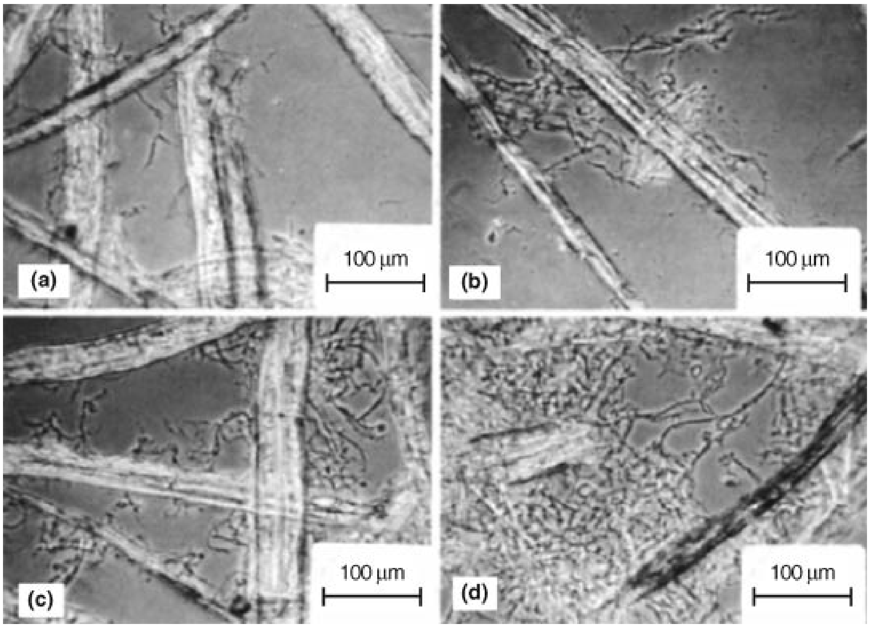

Fig. 4. Optical micrographs of a softwood sulfite pulp (**a**) before beating and (**b**–**d**) after beating in a hollander beater for different periods of time. Beating time increases from (**b**–**d**).

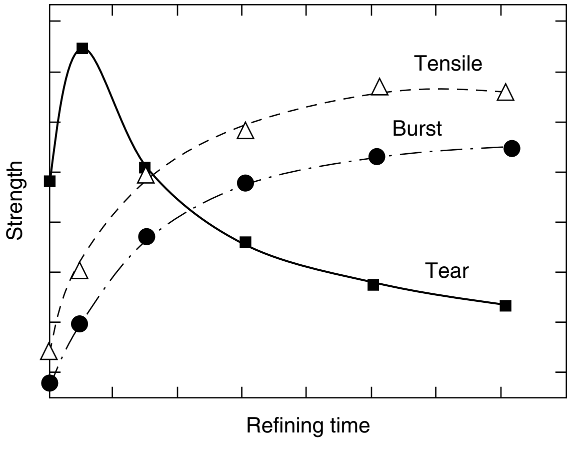

Fig. 5. Beating curves for a softwood kraft pulp.

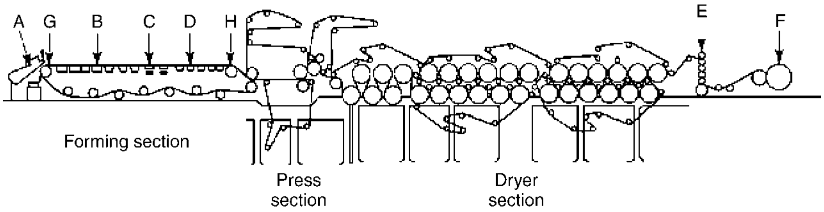

Fig. 6. Fourdrinier paper machine: (A) headbox; (B) Fourdrinier wet end with foil boxes; (C and D) wet and dry suction boxes, respectively, with pickup, and closed transfer of web through the press and dryer sections; (E) calender rolls; (F) reel; (G) breast roll; and (H) couch roll. (Courtesy of Beloit Corp.)

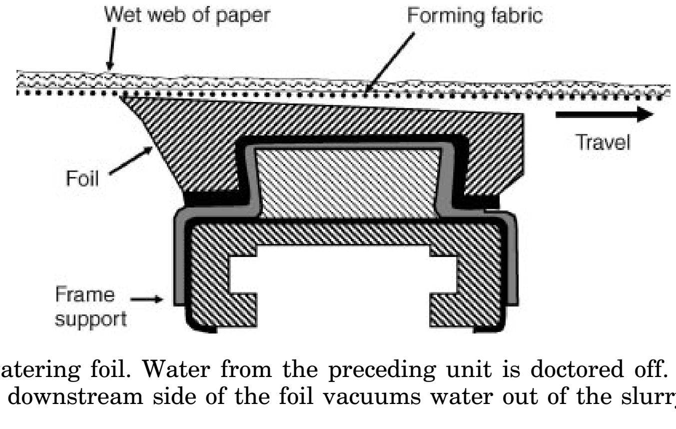

Fig. 7. Dewatering foil. Water from the preceding unit is doctored off. The diverging wedge on the downstream side of the foil vacuums water out of the slurry and through the fabric.

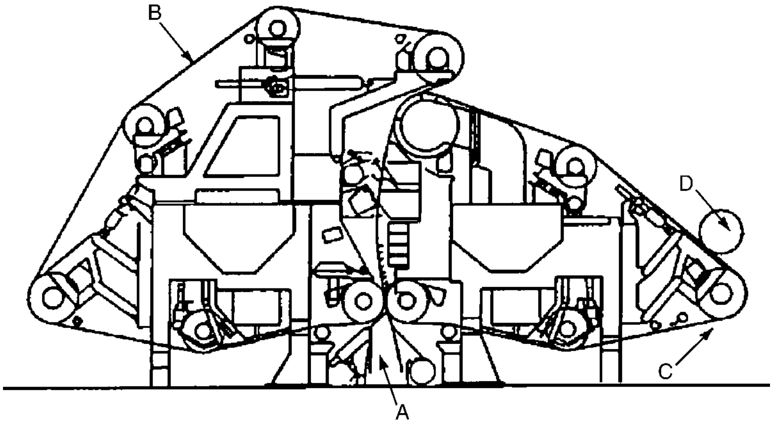

Fig. 8. The Bel Baie II twin-wire former. Stock from (A) the headbox, is formed into sheet between (B) wire number 1 and (C) wire number 2. The web is removed from wire 2 by D, a suction pickup roll. (Courtesy of Beloit Corp.)

Table 1. **Examples of Wood's Chemical Composition**[a]

Fiber types, % Type of tree:	Hardwood (deciduous)	Softwood (conifer)
cellulose,	40	39
hemicellulose,	37	30
lignin,	20	27
extractives,	3	4

[a] Disregarding water.

Table 2. **Typical Examples of Chemical Composition of Papermaking Fibers**[a]

Fiber type, %	Thermomechanical pulp (TMP), %	Unbleached kraft (UBK), %	Bleached kraft (BK), %
yield	96	56	46
cellulose	44	54	78
hemicellulose	26	26	22
lignin	27	10	< 1
extractives	3	< 1	$\ll 1$

[a] Not considering water.

Table 3. **Examples of Typical Compositions of Different Paper Products**

Type of paper	Main type of fibers	Mineral percentage	Starch percentage
newsprint	thermomechanical	0–10	0–1
coated magazine paper	thermomechanical	10–40	2–8
containerboard	unbleached kraft	0–5	0–4
milk carton stock	bleached kraft	0–5	0–1
xerographic copy paper	bleached kraft	10–30	1–5
coated offset printing	bleached kraft	10–35	2–8
tissue paper	bleached kraft	0–5	0

Table 4. **Typical Properties of Paper Fillers**

Filler type	Specific gravity	Refractive index	Particle size, μm	Brightness, %
calcium carbonate:				
ground (GCC)	2.6–2.8	1.56	0.5–3	95–97
precipitated (PCC)	2.6–2.8	1.56	1–2	97–99
kaolin clay	2.5–2.8	1.55	0.5–3.0	80–90
titanium dioxide:				
anatase	3.9	2.55	0.3	98–99
rutile	4.2	2.70	0.3	98–99
talc [14807-96-6]	2.8	1.57	1–10	70–90
synthetic silicates	2.1	1.55	0.1–4.0	93–95

Table 5. **Comparison of Direct, Cationic Direct, Basic, and Pigment Dyes**

	Direct dyes			
Parameter	Anionic	Cationic	Basic dyes	Pigments
dye ion net charge	negative	positive	positive	various
tinctorial strength	moderate	moderate	high	low
brilliancy	moderate	moderate	high	mod.-high
lightfastness	moderate	poor-mod.	poor	excellent
acid, alkali fastness	variable	good	poor	good
water-bleed fastness	good	excellent	good	good
solubility	moderate	moderate	high	insoluble
preferred applications	widely used, all pulp types	fine paper, bleached kraft	high yield pulps	permanent papers
affinity characteristics	usually good; can use fixative	superior affinity	mechanical pulps only	requires retention aid