Kirk-Othmer Encyclopedia of Chemical Technology.

PAPERMAKING ADDITIVES

In papermaking, chemicals can be added either to the pulp slurry prior to sheet formation, ie, internal or wet-end addition, or to the resulting sheet after complete or partial drying, ie, surface or dry-end addition. The method chosen depends on retention and the desired effect. For example, strength additives usually are added internally if uniform strength throughout the sheet is wanted, but they are applied to the surface if the need is for increased surface strength. If an additive cannot be retained efficiently from a dilute pulp slurry, then it is better to apply it to the surface of the sheet.

Papermaking additives can be categorized either as process additives or as functional additives. Process additives are materials that improve the operation of the paper machine, such as retention and drainage aids, biocides, dispersants, and defoamers; they are primarily added at the wet end of the paper machine. Functional additives are materials that enhance or alter specific properties of the paper product, such as fillers (qv), sizing agents, dyes, optical brighteners, and wet- and dry-strength additives; they may be added internally or to the surface of the sheet.

Environmental constraints on the paper industry have resulted in drastic processing changes, primarily because very large amounts of water are used to produce paper. If chemical additives are not efficiently retained in the sheet, in addition to losing the value of these materials, the concentration of these materials increases in the white-water system (the water drained and pressed from the fibers as the sheet is being formed). As paper mills become more closed, ie, as they reuse the white water many times over before treating and discharging it, retention of papermaking additives becomes more critical because the unretained materials also negatively impact the performance of newly added materials as well as the finished sheet. Retention of papermaking additives also becomes more difficult with the increased use of recycled waste fiber and the closing of the water system, because the conductivity and amount of soluble materials increase under these conditions. Some additives become electrostatically neutralized by these materials; others are forced to compete for binding sites on the cellulose fibers.

The U.S. Environmental Protection Agency (EPA) proposed the “cluster rule” for the paper industry in December 1993; it provided detailed and comprehensive guidelines regarding discharges of harmful materials to the air, water, or soil (sludge) (1). The revised Clean Air Act (1990) also identified hazardous air pollutants whose discharge is stringently regulated (2). Numerous regional, state, local, and foreign national regulations exist concerning emissions to air, and discharges to water and sludge. OSHA workplace regulations may have also altered the additive process and the choice of additives.

In addition, many grades of paper and paperboard are used in direct or indirect contact with foods. Thus, many mills only use paper chemicals that have been cleared for use by the U.S. Food and Drug Administration (FDA) (3), so that it is not necessary to segregate machine broke (off-grade paper and edge clippings that are reclaimed for their fiber value) and white water. Most of the chemicals discussed in this article are approved by the FDA for use in paper and paperboard that are intended for applications in food processing and packaging. However, there are various restrictions on both the specific functional uses and amounts of paper chemical additives which can be used, so the FDA status should be confirmed by the supplier before use.

It is also important to study the interactions of papermaking additives (4) in the paper machine water system; some additives act synergistically, so that the performance of each is enhanced by the presence of the other. However, some additives have a negative impact on the performance of other additives, or on other desirable paper properties. Thus, optimization of the addition points and usage rates of the entire additive system is necessary in order to maximize performance of the chemical additives and the paper sheet properties, and to minimize cost and negative interactions both on the paper machine and in the white-water system. This is especially true as unanticipated additives enter the wet end of the paper machine from recycled furnishes, including coated broke (5).

Lists of the manufacturers of each type of product used by the paper industry are available (6). Surveys of chemical suppliers for the U.S. and Canadian pulp and paper industries have been published (7).

1. Process Aids

Process aids, which improve the operation of the paper machine, include retention aids, ie, coagulants and flocculants; drainage aids; effluent treatment for fiber and filler recovery; formation aids; defoamers; wet-web strength additives, pitch-control agents; creping aids; and biocides and slimicides. The first three are phenomenologically related: they act by agglomerating filler particles, fines, or fibers with themselves or with each other. Agglomeration occurs as a result of electrostatic attraction (ie, cationic polymers or alum, known as charge modifiers, neutralized by anionic fibers, fines, or inorganic fillers) or hydrophobic interaction (ie, sparingly water-soluble pitch or defoamer components adhering to dispersed filler particles). Thus, in one papermaking system, an additive may increase first-pass retention, whereas at another mill it would act more as a drainage or dewatering aid (8).

Retention and drainage additives are vital to the use of recycled fibers. Papermakers consider recycled fibers to behave like virgin fines, while recycled fines behave like filler. Drainage on the paper machine can be impeded and first-pass retention reduced by the use of recycled fiber (9). Additionally, the negative impact of contaminants found in recycled fibers can be minimized by the appropriate use of dispersants and other pitch-control additives.

1.1. Retention Aids

Opacifying filler particles usually are ca 0.3–5 μm in diameter and are much smaller than most pulp fibers. Therefore, they are not effectively retained by filtration through the pulp mat as it forms on the machine. In an aqueous suspension, most fillers, like most paper-pulp fibers and fines, develop a negative surface charge which prevents coflocculation of fillers with fines. Retention aids encourage coflocculation by two mechanisms: they neutralize the negative charges on fillers, fibers, or fines so that van der Waals forces can hold them together, and they form molecular bridges between two particles to which they are adsorbed.

Molecular weights of the charge-biasing polymeric retention aids are ca 10^3–10^5. These aids usually contain amine or quaternary ammonium groups and include condensation polymers, eg, diethylenetriamine–adipic acid polyamide [25085-20-5], which are treated with epichlorohydrin [106-89-8] and ammonia—or dimethylamine—epichlorohydrin condensates; ring-opening polymers, eg, polyethylenimine [9002-98-6]; and addition polymers, eg, poly(dimethyldiallylammonium chloride) [26062-79-3] or copolymers of aminoethyl acrylates. These products are supplied as 10–35% aqueous solutions.

The simplest charge-biasing agent is an alum [10043-01-3] which is hydrated aluminum sulfate. The alum referred to in this article is papermakers alum, not aluminum potassium sulfate (see Aluminum compounds, aluminum sulfate and alums). Alum is used to control sheet formation through fiber flocculation, to improve drainage, and to precipitate rosin size. It is used less as a sole retention aid than as an adjunct to other retention aids, especially the bridging types. Alum facilitates adsorption of bridging polymers, eg, by neutralizing negative charges on water-soluble and particulate impurities.

Molecular weights of polymers that function as bridging agents between particles are ca 10^6–10^7. Ionic copolymers of acrylamide are the most significant commercially (see Acrylamide polymers). Cationic comonomers include (2-methacryloyloxyethyl)trimethylammonium salts, diethylaminoethyl methacrylate [105-16-8], and dimethyldiallylammonium chloride [7398-69-8]; anionic comonomers include acrylic acid [79-10-7] and its salts. Both types of polyacrylamides, but especially the anionic, can be more effective in the presence of alum (10, 11). Polyethylenimine and vinylpyridine polymers, eg, poly(1,2-dimethyl-5-vinylpyridinium methylsulfate) [27056-62-8] are effective but are used less frequently.

The high molecular weight bridging polymers are more effective retention aids than the lower molecular weight, charge-biasing materials. However, the former cannot be shipped economically, except as solids, because of their high solution viscosities. These solid products must be dissolved with care to prevent the formation of slowly dissolving lumps. Invert emulsions, ie, aqueous polymer solutions that are emulsified in a solvent, and logs of water-swollen, super-high molecular weight ($>10^7$) polymer have been introduced to circumvent problems of solution makeup. The lower molecular weight, charge-biasing polymers are sold as solutions and can be diluted easily.

Synergistic improvements in filler retention have been achieved through the use of combinations of additives, in which addition of a low molecular weight cationic polymer, often referred to as a coagulant, is followed by that of a high molecular weight anionic polymer, or flocculant (11). These probably function through a combination of charge biasing and bridging. Although they provide very high retention of fillers and fines, these combinations can disrupt formation by overflocculating the fibers (12). Such overflocculation can be compensated for by redispersing the flocs with vigorous agitation of the stock just before it passes onto the forming wire (13). It has been found that the addition of a high molecular weight cationic flocculant prior to a point of shear, followed by a medium-to-high molecular weight anionic flocculant, improves fines and filler retention without impeding drainage (14, 15).

Another type of dual-retention system has emerged; in these systems, a synergistic combination of a small, inorganic particle and a polymer enhances retention. These microparticulate retention systems are composed of a high molecular weight cationic flocculant and an anionic particle. The most common of these systems consist of combinations of cationic starch with anionic aluminum hydroxide or colloidal silica, or high molecular weight cationic polyacrylamides with bentonite or colloidal silica (16). The cationic polymer flocculates the fines, fillers, and fibers. The anionic microparticle, added after shearing the suspension, is believed to reflocculate or strengthen the previous flocs, owing to its high specific surface and anionic charge. The anionic microparticle, because of its small size, appears to increase the density of the flocs, thus reducing their size (17). Unlike purely polymer-based dual retention systems, the microparticle systems are reversible, in that the floc system reverts to its original structure once shear is removed (18).

The percent retention of mineral fillers usually is measured directly by ash analysis of the sheet, with appropriate corrections for weight loss of the particular filler during ashing. During production, it can be calculated by difference from the solids content of the white water. The opacifying power of a filler depends on its distribution in the sheet. A finely divided filler that is distributed uniformly on fibers opacifies paper more effectively than the same amount of filler that is distributed in fewer, larger aggregates. The scattering coefficient, a measure of the optical efficiency of the retained filler, is calculated from the basis weight, ie, the sheet weight per unit area, and reflectance of sheets against white and dark backgrounds using the Kubelka-Munk equation (19) or derived forms (20–22). The efficiency of a retention aid depends on the amount added, the shear, and the molecular weight. An overdose of retention aid can redisperse the filler.

Retention can be studied as a function of both dose and shear in the dynamic drainage jar (DDJ), in which a variable-speed agitator exposes the stock to controlled shear and prevents mat formation during drainage (23). Thus, the shear dependence of retention, which results from electrokinetic and colloid effects, can be studied, as distinct from retention resulting from filtration on a fiber mat. The degree of shear on a given paper machine can be quantified as an rpm-equivalent in the drainage jar by varying the agitator speed in the DDJ test for a given stock furnish until the percent retention equals that on the paper machine.

Salts, eg, alum or calcium chloride [10043-52-4], and cationic polyacrylamides are effective retention aids in bleached and unbleached kraft pulp.

1.2. Formation Aids

The repulsion of negatively charged fibers in water is not always sufficient to prevent all flocculation, which can result in uneven fiber density in paper. Dispersants can prevent flocculation prior to immobilization of the wet fiber mat on the wire. Polyacrylamide [9003-05-8], poly(ethylene oxide) [25322-68-3], and natural gums, eg, guar gum [9000-30-0] and locust bean gum [9000-40-2], promote even fiber distribution. High molecular weight anionic polymers, such as polyacrylates, lignin sulfonates, and naphthalene sulfonates, can also act as dispersants and enhance sheet formation, but they may impede drainage in some systems (24).

1.3. Drainage Aids

The break-even point in a typical paper mill is high, ie, ca 85% of capacity. Therefore, small increases in productivity can cause large increases in profits and can postpone the massive capital investment, ie, $>\$500 \times 10^6$ required to build a new paper machine. For machines where dewatering on the Fourdrinier wire is the slow step, dewatering or drainage aids can effect faster machine operation and, therefore, can increase production (25). However, a drainage aid can improve drainage on one section of the machine and impede it on another (8). For example, high molecular weight cationic flocculants can accelerate initial percolation of water on the wire by flocculating the pulp and allowing channelling, but further dewatering on the machine suction boxes is impeded by air leakage through the channels, which reduces the pressure gradient (26). Thus, an ideal drainage aid alters the surface properties of the fibers so that they hold less water, and limits the amount of fiber flocculation. This balance of properties can be achieved by combining a drainage aid with sufficient agitation to redisperse the fiber flocs immediately prior to sheet formation.

1.4. Defoamers

Foam is a common problem in papermaking systems (27). It is caused by surface-active agents which are present in the pulp slurry or in the chemical additives. In addition, partially hydrophobic solid materials can function as foam stabilizers. Foam can exist as surface foam or as a combination of surface foam and entrained air bubbles. Surface foam usually can be removed by water or steam showers and causes few problems. Entrained air bubbles, however, can slow drainage of the stock and hence reduce machine speed. Another serious effect is the formation of translucent circular spots in the finished sheet caused by permanently entrained air.

Defoamers (qv) are available in several forms, composed of many different materials. Historically, paste and solid defoamers were used extensively. Composed of fatty acids, fatty amides, fatty alcohols, emulsifiers (and mineral oil [8012-95-1] in the high solids paste emulsions), these defoamers required emulsification (brick) or dilution (paste) before use. Liquid defoamers have become the preferred form, insofar as concern about handling and overuse have been overcome.

Some liquid defoamers are preemulsified relatives of paste defoamers. In addition to the fatty components mentioned above, kerosene [8008-20-6] or an organic cosolvent such as 2-propanol have been used to enhance stability of the oil—water emulsion and the solubility of the defoamer's active ingredients. These cosolvents are used less frequently as concerns increase about volatile organic emissions (VOCs) from the paper machine. Additionally, the use of ultrapure mineral oil in defoamers has become commonplace. Concern about the creation of 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) in the pulping process has led to the discovery of unchlorinated precursor molecules, especially in recycled mineral oil and other organic cosolvents used in defoamer formulations (28). In 1995 the mineral oil that is used is essentially free of dibenzodioxin and dibenzofuran. In addition, owing to both the concern about these oils and the fluctuating cost of raw materials, the trend in paper machine defoamers is toward water-based defoamers (29).

The defoamer formulations mentioned so far consist of fairly inexpensive raw materials, but several more costly defoaming materials have come into use in paper mills. Hydrophobicized silica particles are useful in some emulsion formulations. Silicone solutions and emulsions are very effective in eliminating foam in paper machine water systems. The silica- or silicone-based defoamers have higher activity, which somewhat compensates for the higher cost, but care must be taken to prevent overuse.

1.5. Wet-Web Strength Additives

When the wet sheet is transferred from the forming wire to the press section of the paper machine, it still contains 60–75% water. If there is inadequate sheet strength, breaks occur, resulting in machine downtime and lost production. A number of water-soluble chemical additives have been shown to enhance wet-web strength, including synthetic, eg, anionic polyacrylamides, and natural, eg, locust bean and guar gum, polymers. Several modified natural polymers have also shown promise, including chitosan (30), blocked reactive group starches with acetal protected aldehydes (31), and cationic aldehyde starches produced from them (32). These have replaced the previously successful dialdehyde starch which is made in Japan (31). Since these additives improve wet-web strength indirectly by improving formation and accelerating water removal from the forming sheet, other formation and drainage aids may also improve wet-web strength.

1.6. Pitch Control Agents

Sticky pitch deposits may form at various locations at the wet end of the paper machine. If these deposits enter the system they may be incorporated in the sheet, which could result in sheet breakage or off-color spots. Historically, the main source of pitch in a papermaking system was the natural wood resins that remain in the virgin pulp. In addition, with the use of increased levels of recycled fibers as a significant portion of the papermaking furnish, other sticky materials, eg, resins, adhesives, waxes, inorganic fillers, and latexes called "white pitch" and "stickies," which are especially troublesome when utilizing coated broke (33), may contribute to pitch problems. Pitch problems can be minimized by more thorough pulp washing and screening, which, however, may not be practical, insofar as the water systems in paper mills are increasingly more closed.

The most widely used pitch control method is the addition of pitch dispersants, which can be either organic, ie, typically anionic polymers such as naphthalene sulfonates, ligninsulfonates, and polyacrylates (33, 34), or inorganic, ie, typically clay or talc. The polymers maintain the pitch as a fine dispersion in the pulp, preventing agglomeration and potential deposition on the paper machine or the sheet. When talc, clay, or other adsorbent fillers are added to the furnish, moderate amounts of pitch can adsorb on these materials, producing a nontacky solid that can be retained in the sheet.

Low molecular cationic polymers or alum can also be used to flocculate pitch, ie, bind up the pitch so that it is retained in the sheet, to minimize pitch deposition on machine surfaces and fabrics (35, 36). Alum is used commonly in newsprint operations (34). The addition of a nonionic surfactant with a hydrocarbon solvent to the wet end has shown some utility in preventing deposits of adhesive recycled furnish contaminants from forming on the paper machine (37).

1.7. Effluent Treatment

Like the mineral- and pigment-processing industries, the paper industry must minimize the amount of suspended solids in mill effluents. Save-alls, which are specific to the paper industry, are designed to recover paper fines and filler particles for recycle to the paper machine. Flocculants are used both in the paper machine furnish to increase retention of fines and fillers in the sheet (38) and in save-alls to help recover finely divided solids, both organic and inorganic, from the white water. Alum is used widely as a coagulant for effluent treatment in paper mills. Most of the low and high molecular weight polymers, which serve as retention aids, also can be used as coagulants and flocculants (see Flocculating agents).

1.8. Slimicides and Biocides

Most paper machine systems are ideal environments for the growth of slime-forming bacteria and fungi because of the many nutrients which are present, eg, hemicelluloses, starches, and other organic additives, and because temperatures often are optimum for microorganism growth. The most effective way to prevent slime formation is to maintain cleanliness in the entire papermaking system. However, in most mills, cleanliness is not sufficient to completely prevent slime formation. Therefore, slimicides and biocides are frequently added at various points in the papermaking process. This is of crucial importance when the paper is produced for food contact or medical applications.

There are two categories of biocides in use in paper mill systems: oxidizing biocides, including chlorine, hypochlorite, hypobromous acid, and chlorine dioxide, and nonoxidizing biocides, ie, methylene bisthiocyanate, carbamates, and quaternary ammonium compounds (39). When alkaline paper is produced, biological growth can be a serious problem; maintaining a residual free chlorine level (0.3–0.5 ppm) in the process water has been recommended (33). Because of the specificity of the effectiveness of these materials (40), it is best for paper mill personnel to work closely with biocide suppliers to select the best control agent for a given situation (see Industrial antimicrobial agents).

1.9. Creping Aids

Disposable sanitary papers, which are used in napkins, towels, and facial and toilet tissue, should absorb water. Although surface-active agents and some strength resins can improve absorbency, the more prevalent method involves mechanically creping the sheet. Mechanical creping simultaneously improves softness and absorbency. Creping is achieved by peeling the sheet from a steel drier roll with a sharpened doctor blade, which is maintained at an angle to the surface of the roll. Successful creping depends on the angle and design of the doctor blade and the degree of adhesion of the sheet to the roll. If the sheet adheres excessively, too much dry strength is lost as the sheet is chiseled from the roll. Principal creping adhesives include animal glues, starch, neutral-cure wet-strength resins, specialized polyamines, and high molecular weight retention aids. Among the agents that can be added to facilitate release from the roll are emulsified paraffin oil [8012-95-1], silicone oils, or poly(ethylene glycol)s (41). Proprietary combinations of polyamide—epichlorohydrin resins and release agents sometimes are used to tailor the proper balance of adhesion to release for a given pulp on a given machine, at a given sheet moisture content. Residual hemicellulose in the pulp affects adhesion significantly.

2. Functional Internal Additives

2.1. Sizing Agents

Paper sizing provides paper and paperboard with resistance to wetting by liquids. Because aqueous fluids, eg, ink, water, and milk, generally are the liquids of concern, the usual purpose of sizing is to produce water repellency. Most grades of paper that are to be printed or written on are sized so that the ink does not spread laterally or feather. For other uses, it is necessary to size paper to prevent penetration by liquids, eg, in paper cups, milk cartons, and packaging papers and boards (see also Waterproofing and water/oil repellency).

The contact angle formed between water and the paper surface is the primary factor determining the extent of wetting, as shown in Figure 1 (42). Well-sized paper has an initial contact angle of 91–100°, which

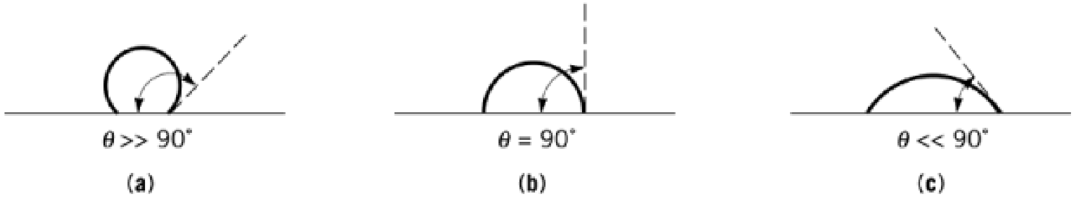

Fig. 1. Physical phenomena governed by contact angle: (**a**) extremely limited wetting and spreading, tendency to retract, does not penetrate; (**b**) limited wetting and spreading, no tendency to penetrate; (**c**) extensive wetting and spreading, strong tendency to penetrate.

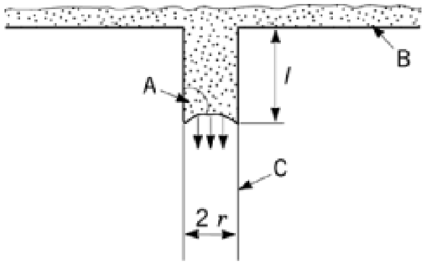

Fig. 2. Liquid flow-through capillary (Washburn equation). Time rate of penetration=$dl/dt=1/4[\gamma/\eta]\times[r/l]\times\cos\theta$, where γ=surface tension and η=viscosity. A, contact angle θ between liquid and capillary wall; B, penetrating liquid; C, partially filled capillary, r=radius, and l=length already filled.

permits only limited wetting and spreading; there is no tendency for water to penetrate through pores. However, if the contact angle is considerably less than 90°, water wets, spreads, and penetrates the sheet quite rapidly. When properly oriented on the fiber surfaces, purely hydrophobic materials such as wax, and amphipathic, ie, polar—nonpolar, materials such as rosin[8050-09-7] provide a low surface energy coating which gives the high contact angle necessary for sizing.

The rate of flow of a liquid through a very thin tube or capillary is represented in Figure 2 by the Washburn equation, which combines the equation representing the natural driving force for fluid movement in a capillary tube with the Poiseuille equation for laminar flow through a tube (43). Two of the five parameters that govern the rate of flow, ie, surface tension and viscosity of the penetrating liquid, are determined by the customer's needs, ie, the liquid whose movement the sized paper product should resist. Two more, ie, the radius and length of the pores, are governed by the papermaker's products, ie, the basis weight, bulk density, and porosity of the sheet. Thus, the chemical supplier can vary only the composition of the sizing agent to give the contact angle needed to produce the sizing that is required by the paper producer and consumer.

2.1.1. Rosin-Based Sizes

These sizes are normally provided in one of three forms: paste, liquid and emulsion.

Paste rosin sizes are supplied as viscous pastes containing 60–80% solids. These sizes may contain unmodified or fortified rosin that has reacted (ie, been fortified) with either maleic anhydride [108-31-6] or fumaric acid [110-17-8] (see Fig. 3). In either case, the unmodified or fortified rosin is treated with aqueous alkali so that the degree of neutralization, ie, saponification, varies from 75–100% depending on the physical state desired for the commercial product. Before use, the paste size must be converted to a stable, dilute rosin size emulsion by careful sequential dilution with warm water followed by cold water, with good agitation.

Liquid rosin sizes are based on more highly fortified rosin than those used in paste sizes. The highly fortified rosin is then neutralized 100% with aqueous alkali. These sizes are very low viscosity liquids typically

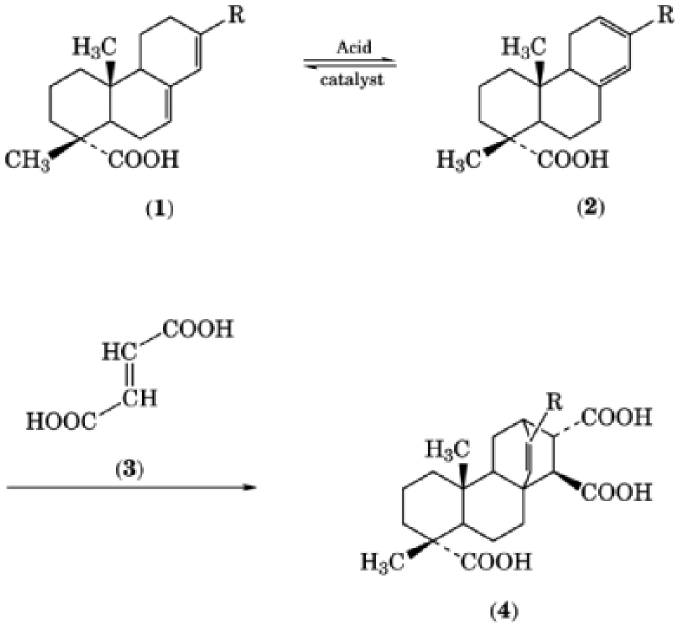

Fig. 3. Resin acids in rosin sizes, R= $CH(CH_3)_2$. The rosin acids are represented here as abietic acid [514-10-3] (**1**) and levopimaric acid [79-54-9] (**2**). In rosin there are other isomers and disproportionation products. The product of reaction with fumaric acid (**3**) is levopimaric acid—fumaric acid adduct [77942-79-1] (**4**).

in the 45–55% solids range. The advantages that liquid sizes have over paste sizes lie in their handling and sizing efficiency. Due to its lower viscosity, liquid size can be used directly without emulsification or can be simply diluted with cold water, thus eliminating the need for heated storage and emulsification equipment. Since they are highly fortified, liquid sizes generally require lower usage rates than paste sizes to achieve a specific degree of sizing.

Fortified rosin can also be converted to high free-rosin emulsions by using various stabilizers. Typically, these are 35% solids emulsions, which exhibit excellent stability in relation to storage and mechanical action, such as is found in transfer pumps. Generally, fortified rosin emulsions are more efficient sizes than their soap-based liquid or paste counterparts.

Rosin sizing usually involves the addition of dilute aqueous solutions or dispersions of rosin soap size and alum to a pulp slurry (44–46). Although beater addition of either coreactant is permissable, addition of both before final pulp refining is unwise because subsequently exposed cellulose surfaces may not be properly sized. The size and alum should be added sufficiently early to provide uniform distribution in the slurry, and adequate time for the formation and retention of aluminum resinates, commonly referred to as size precipitate. Free rosin emulsion sizes, however, do not react to a significant degree with alum in the pulp slurry, and addition of a cationic starch or resin is recommended to maximize retention of size to fiber. Subsequent reaction with aluminum occurs principally in the machine drier sections (47).

These rosin-based sizes, whether paste, liquid, or emulsions, can be used to size all grades of paper that are produced at acid pH. The latter include bleached or unbleached kraft linerboard and bag paper, bleached printing and writing grades, and cylinder board. In addition, polyaluminum compounds have been used in place of alum, most notably, polyaluminum chloride (48), which can reduce barium deposits where these have been a problem. The barium chloride by-product is more water-soluble than barium sulfate. Other polyaluminum compounds such as polyhydroxylated forms of alum and polyaluminum silicosulfate have been evaluated as alum replacements.

Rosin sizes, most notably emulsion sizes, have gained increased usage in grades of paper produced at neutral pH. The principal advantage of neutral papermaking is that it allows increased usage of recycled white paper and machine-coated broke that contains calcium carbonate filler, and therefore would require operating at a higher pH to avoid the sizing and machine runnability problems associated with soluble calcium and volatile carbonate, which produces extensive foaming at an acid pH (49).

2.1.2. Cellulose-Reactive Sizes

There are two principal types of synthetic paper sizes that owe their effectiveness to the hydrophobic size molecule actually forming a covalent bond with the cellulose (50). The first cellulose-reactive sizes were based on hydrolytically stable emulsions of alkylketene dimers (AKD) of long-chain fatty acids. More recently, cationic AKD emulsions have been developed that produce more rapid on-machine sizing during drying than the original unmodified products (51). The other significant cellulose-reactive internal sizing additive is alkenyl succinic anhydride (ASA), made by reaction of a long-chain alkene with maleic anhydride. Since ASA hydrolyzes rapidly in water, it is shipped neat and emulsified on-site (52).

Cellulose-reactive sizes have gained prominence because paper can be sized effectively at neutral to alkaline pH with these additives. There are several advantages to sizing paper under slightly alkaline conditions. Inherently, paper formed under alkaline conditions has greater strength than paper formed under acid conditions. This allows for a greater substitution of lower cost filler for higher cost (but higher strength) fiber. Calcium carbonate is useful as a pigment and filler only on the alkaline side. Because paper that is made under alkaline conditions has greater strength, it can be made from a less highly refined furnish which requires less energy for refining and drying. Another significant advantage of alkaline papermaking is the reduction of inorganic salts in the white water, which reduces the cost of effluent treatment and permits greater closure of the white-water system. Alkaline papermaking can result in increased productivity because of lower maintenance cost than had previously been needed owing to acid wear of machine parts, but the abrasiveness of the calcium carbonate pigments causes increased wear on paper machine synthetic wires and other parts (51). Paper formed at an alkaline pH also has greater permanence than acid paper (ie, its strength is retained better over time), and it has thus become important for archival purposes (53).

Alkaline sizing agents are especially effective in milk-carton board and printing and writing grades that utilize calcium carbonate fillers.

2.1.3. Other Internal Sizing Additives

Wax emulsions have been widely used to impart special resistance to functional penetrants, such as oil, grease, and blood. Butcher paper, meat wrap, cable wrap, bleached kraft foodboards, and folding boxboards are all paper grades that have utilized wax emulsions to develop a high degree of sizing at minimum cost. However, the use of AKD sizes and high efficiency, rosin-based emulsion sizes has caused a reduction in the use of wax emulsions. Most wax emulsions that are used for internal addition are stable to mild acid and mild alkali. They are retained in the sheet as a result of the addition of alum, which breaks the emulsion; the wax particles are then retained by filtration. Wax emulsions that can be broken by the addition of acid are used to a lesser extent. Cationic emulsions are used to a limited extent; they are retained by addition of sulfate ions to break the emulsions. In general, wax emulsions are added to the pulp furnish after addition of rosin-based size and alum, and just prior to the paper machine headbox.

Fluorochemicals have been used in the manufacture of oil-resistant paper and paperboard, and other specialty grades. The fluorochemicals that are best suited are characterized by a long perfluorocarbon chain attached to either a functional group or a polymer backbone. Suitable fluorochemicals include fluorochemical chrome complexes, fluorochemical copolymers, and fluorochemical phosphates; the latter are the most commonly used, since they are approved by the FDA for direct food-contact packaging. These products, provided as 33 wt % solids solutions in water with an organic cosolvent, can be retained efficiently by the use of cationic retention aids. Although fluorochemicals provide excellent oil and grease resistance, they do not provide sizing against aqueous penetrants. When both oil and water resistance are desired, the fluorochemical phosphates usually are used with AKD sizes.

2.1.4. Mechanism

The general mechanism of effective sizing involves the following sequential steps. (*1*) Efficient retention of the sizing agent in the sheet, preferably as tiny particles. (*2*) Uniform distribution of sizing agent over fiber surfaces. If the size has not been retained in appropriately small, well-distributed particles, sizing distribution must result from spreading during drying. (*3*) Firm anchoring to fiber surfaces so that impinging liquids do not overturn the molecules which present a hydrophobic surface to the exterior. Ideally, the sizing agent should be chemically inert to the liquids which are encountered in use and should not adversely affect other paper properties.

Aluminum resinate particles, ie, size precipitate, are attracted to the fiber surfaces because of a difference in charge and thus are retained (45, 46, 54). In general, the particles of size precipitate are small and are distributed fairly uniformly over the sheet. However, on drying, there is some sintering of the particles which helps to redistribute them on the fibers.

The higher efficiency of fortified rosin sizes is believed to result from the semihydrophilic nature of the rosin adduct molecules, which results in a more dispersed system of particles during size precipitation by alum. Consequently, there is a more uniform distribution of somewhat smaller particles on the sized fibers. This dispersing effect may result from the strong tendency of aluminum to coordinate with organic anions.

During drying, the lower softening point of the size precipitate, which is obtained from high free-rosin emulsion sizes, permits much greater redistribution of the retained sizing agent than is possible with ordinary rosin size and fortified rosin size. It is postulated that the free rosin acids in the retained size precipitate react directly with various aluminum compounds during drying of the sheet to provide the anchoring required for good sizing. After drying, the aluminum resinates are immobile below 100°C and are oriented with the hydrophilic carboxyl groups combined with aluminum on the fiber surface, and the hydrophobic bulk of the rosin molecule oriented outwardly.

Synthetic cellulose-reactive sizing agents, such as long-chain alkylketene dimers and alkenyl succinic anhydride, are added to the pulp slurry as emulsions and are retained in the sheet by cationic retention aids (cationic polymers or cationic starch), which also may serve as part or all of the emulsifier system. The retained sizing agent has a low softening point, a property which permits it to distribute uniformly over fiber surfaces during drying. The size also reacts with hydroxyl and carboxyl groups on the cellulose fiber surface to form esters and anhydrides, which firmly anchor it to the paper surface. As the paper dries, there is a competing reaction of the size with water, which renders some of the sizing agent ineffective.

In the production of alkaline paper, a phenomenon called size reversion, ie, paper that possesses the appropriate level of sizing response when produced then loses all or part of that sizing response upon aging, can sometimes be observed. Several factors appear to be at work. The use and overuse of polyamines and other promoters that enhance the on-machine sizing response of AKD can also promote the hydrolysis of AKD as the paper ages, with a potential loss of sizing (55). The use of highly alkaline calcium carbonate filler slurry can cause a similar loss in the sizing response over time, for both AKD- and ASA-containing sheets (55, 56). The effect is not seen in paper filled with clay alone, unless the papermaking slurry is made excessively alkaline. With all sizing agents (acid or alkaline), sizing is most efficient if the size is retained on the fiber surfaces, as opposed to the filler surfaces (44, 57).

2.1.5. Sizing Tests

A thorough description of sizing tests can be found in Reference 58. No one test is unanimously endorsed or entirely satisfactory. A practical sizing test should either measure end use requirements directly, simulate use conditions, or correlate with use requirements. A reliable test also should be sensitive to small changes in sizing level and be reproducible from one operator to another. In printing and writing grades of paper, end use printability tests are increasingly being utilized, as opposed to continuing to try to correlate size tests which mimic the penetration of ink solutions. One printability test that is increasing in popularity with uncoated free sheet manufacturers is the ink jet printability test. This test can be performed with either a black-and-white or color printer. Key components of the test include show-through, feathering, spreading, resistance to smear when highlighted with both acid and alkaline highlight markers, and color-to-color bleed. This test is a more accurate predictor of paper performance than other size tests.

2.2. Dry-Strength Additives

An increasing amount of dry-strength additives is being used. This expanded use is driven largely by the need to utilize higher levels of weaker fiber sources, ie, recycled paper and paperboard. Modified starches are the most widely used, with the cationic and amphoteric starches dominant for wet-end application. Polyacrylamides, both anionic and cationic, are the most important of the synthetic dry-strength additives, and are used in a variety of grades. Vegetable gums, both natural and modified, and sodium carboxymethylcellulose [9004-32-4] (CMC) are also widely used.

2.2.1. Utility

Increased sheet strength through increased fiber refining generally results in an increase in sheet density. This means that increased sheet strength is accompanied by a reduction in density-related properties, such as opacity, porosity and bulk. Dry-strength additives increase sheet strength with little or no change in sheet density (59). This provides for faster drainage during paper formation, and allows for separate optimization of sheet strength and density-related properties. In addition to increased sheet strength as a direct objective, the dry-strength additives permit benefits, that would otherwise be strength-reducing, to be exploited. These include reduced refining energy, higher filler levels, increased use of weaker, less expensive fibers, and reductions in basis weight.

2.2.2. Natural Gums

The mucilages from plant roots and stems, most notably guar gum, locust bean gum, and tamarind gum, may be used by papermakers to improve the strength of paper (60). Galactomannan is the effective natural polymer in the materials. These gums, of which guar is the most commercially available, tend to be irreversibly adsorbed on cellulose pulp fibers and thus augment the hemicelluloses (qv) formed during refining to impart strength to the paper. Cationic and amphoteric guar derivatives have been produced and used as strength additives; in some applications, these derivatives are more effective than the naturally occurring gums. Gums are prepared as aqueous solutions before addition to the pulp slurry for ease of handling. In general, gums are used at 0.1–1.0 wt %, based on the dry pulp fibers (see Gums).

2.2.3. Starches

Like the natural gums, starches were among the first strength additives used. Both cereal starches, such as corn and wheat, and root starches, eg, potato, are effective, along with numerous types of modified starches. Anionic starches enhanced by carboxylation or phosphorylation, cationic starches produced by addition of tertiary amino or quaternary ammonium cationic groups, amphoteric starches containing both cationic and anionic functionalities, and starches modified with synthetic polymers are all widely used. Cationic starches modified by the addition of an acetal group (blocked aldehyde) can also serve to enhance the dry strength of paper (61).

Like the natural gums, starches need to be cooked in water to form dispersions for addition to the papermaking system. Various techniques have been developed for cooking starches rapidly (see Starch). In general, anionic starches are used with alum, which aids in starch retention. The cationic and usually the amphoteric starches are self-retaining.

Starches used to increase the internal strength of paper as measured by tensile, edge crush resistance, Mullen burst, and Scott bond strength are added at the wet end, whereas starch used to increase surface strength as measured by pick and resistance to linting are added at the size press.

2.2.4. Cellulosics

Carboxymethylcellulose (CMC) is the principal cellulose derivative used as a strength additive in papermaking. Like the anionic starches, CMC usually is used in alum-containing systems. When used in this way, CMC is about as effective a strength additive as the anionic acrylamide polymers. Carboxymethylcellulose also can be used with cationic, water-soluble, wet- and dry-strength additives. For example, when CMC is used with an aminopolyamide—epichlorohydrin wet-strength resin, increased wet and dry strength and sometimes a more uniform coating on Yankee dryers are achieved (see Cellulose ethers).

2.2.5. Acrylamide Polymers

In the early 1950s, anionic and cationic polyacrylamides were introduced as strength additives for paper (62). The advantage of these synthetic polymers over starches and natural gums is the ease with which molecular weight and degree of substitution of anionic and cationic groups can be varied. In general, the anionic acrylamide polymers, usually using acrylic acid as the comonomer to impart the negative charge, are used in alum-containing systems. In addition to improving the strength of paper, the acrylamide polymers often provide improved retention of fillers, improved rosin-sizing efficiency, faster drainage of the stock on the wire, and easier drying of the sheet.

The cationic acrylamide polymers may contain either tertiary amine or quaternary ammonium groups. Because of their positive charge, they are self-retaining on pulp fibers; therefore, they can be used effectively in nonalum systems.

Combinations of anionic and cationic resins are used. Some of the early systems involved the use of a cationic wet-strength resin with an anionic dry-strength additive to provide both increased wet and dry strength (63). Combinations of anionic and cationic dry-strength additives also are used to provide strength effects which cannot be achieved by using either polymer alone (64). The ratio of the two polymers must be optimized to achieve maximum performance (see Acrylamide polymers).

2.2.6. Mechanism

The principal effect of a dry-strength additive is to improve the degree of bonding between fibers. Chemical strength additives provide, at least in part, the same effects as additional refining. In some cases, an additional effect is obtained and is comparable to that resulting from the use of stronger fibers. Of the total improvements in tensile and burst strengths, which are produced by locust bean gum, 60% are attributed to increased bond strength, 25% to improved sheet formation, and 15% to formation of new bonds (65). Thus, 75% of the dry-strength improvement is directly related to improved bonding. Apparently the effect of a dry-strength additive is to provide extra adhesive for fiber bonding. This probably results from increasing the degree of the bonded area at each fiber—fiber crossover point as well as the frequency of bonding per unit fiber length. For example, the treatment of a paper sheet with a starch solution increases both the optical contact area per crossover region and the frequency of optical contact areas along the fiber. Further refining produces both of these effects. Thus, the addition of a dry-strength additive provides additional water-soluble polymeric adhesive to help bond the individual fibers.

2.3. Wet-Strength Additives

The dry strength of paper can be augmented by natural and synthetic polymers whose hydrogen-, ionic-, or covalent-bonding capabilities enhance the hydrogen bonding that already exists between cellulose fibers. In the presence of water, the cellulose hydrogen bonds are disrupted, and the paper does not have an appreciable amount of wet strength, ie, strength in the presence of water. With few exceptions, wet-strength additives (66) are capable of covalently bonding in order to preserve paper strength in the presence of water. Tissue and toweling, linerboard, medium, carrierboard, and bleached carton are some of the principal grades that require an amount of wet strength to be functional.

2.3.1. Urea—Formaldehyde and Melamine—Formaldehyde Resins

The first wet-strength resins were thermosetting urea—formaldehyde (UF) resins [9011-05-6] added at the wet end of the paper machine and cured in the drier section to produce paper with permanent wet strength. Anionic groups were incorporated in the UFs to enable them to be precipitated onto pulp with alum. Later, cationic UFs were produced by the addition of polyamines, such as diethylenetriamine [61472-52-4], that were self-retaining. Similarly, heating melamine (triamino-*s*-triazine) with three equivalents of formaldehyde yields trimethylolmelamine [1017-56-7] which, when treated with hydrochloric acid, forms a colloidal wet-strength resin. Both UF and melamine—formaldehyde (MF) resins are acid-curing, ie, their use requires mineral acid or, preferably, alum to catalyze the thermosetting reaction. On a weight basis, melamine resins can impart higher wet and dry strength than can UF resins. MF resins with lower residual (free) formaldehyde content, and hence lower subsequent emissions in the papermaking process, have been developed (67) (see Amino resins and plastics).

2.3.2. Aminopolyamide—Epichlorohydrin Resins

If tissue and toweling is produced at a neutral-to-alkaline pH, the paper is softer and more absorbent which are desirable qualities for these grades. Thus, the aminopolyamide—epichlorohydrin resins, which cure most efficiently at neutral-to-alkaline pH, were readily accepted in these markets. In addition, these resins are effective creping aids in absorbent papers and allow for production of wet-strengthened paper without the negative aspects of acid-catalyzed degradation and embrittlement of the paper, and machine corrosion. As concerns grew about formaldehyde in the workplace, the use of aminopolyamide—epichlorohydrin resins surpassed UF and MF resins, eventually almost completely replacing them. The last grades to convert to polyamide resins were the high basis weight, unbleached grades which were difficult to repulp when wet-strengthened with polyamide resins. UF and MF grades repulp fairly readily; the repulping of polyamide-containing paper can be assisted by oxidants such as hypochlorite, which are, however, readily consumed by the lignin in unbleached fiber.

2.3.3. Polymeric Amine—Epichlorohydrin Resins

Various wet-strength resins have been produced utilizing still bottoms containing bishexamethylenetriamine [143-23-7], ie, by-products of hexamethylenediamine production. Like the aminopolyamide—epichlorohydrin resins, these resins are also neutral-to-alkaline curing, and their lower performance is offset by their lower cost. More recent polyamine—epichlorohydrin resins have been based on the use of poly(methyldiallylamine) [55553-13-4]. As these resins are provided in a storage-stable chlorohydrin form, they require alkaline activation to produce reactive epoxides, prior to use. They can be more efficient than the polyamide—epichlorohydrin resins, providing higher dry strength and dimensional stability on water immersion, although they can also be more difficult to repulp.

2.3.4. Aldehyde-Modified Resins

Polymers containing reactive aldehyde groups, as distinguished from those made with formaldehyde and containing methylol groups, are characterized by good absorbency, high dry-strength efficiency, and fugitive wet strength, which makes them more suitable for sanitary papers than packaging grades. The wet strength that is provided by aldehyde-modified resins decreases faster and further, to below one-third its initial value after prolonged soaking, than that imparted by amino polymer—epichlorohydrin resins. Commercial versions of these temporary wet-strength resins include cationic polyacrylamide-glyoxal resins and cationic blocked aldehyde starch dispersions (31, 32). These resins are most efficient at lower pH, especially in the presence of alum, but can develop wet strength in paper as high as pH 6.0–6.5.

2.3.5. Mechanism of Wet-Strength Development

There are two predominant theories that attempt to explain the mechanism of wet-strength development in paper. The protection theory proposes that the wet-strength resin forms a restraining network, by cross-linking either with itself or bonding with the cellulose. Thus, the network protects a fraction of the hydrogen bonding in the dry sheet by limiting the swelling of the cellulose and hemicelluloses in the presence of water. Alternately, the reinforcement theory proposes that the new covalent bonds formed by the wet-strength resin are the ones that remain unbroken by water.

In support of the protection theory are observations that, in the curing reaction, urea–formaldehyde resins have approximately the same activation energy on a variety of substrates, including glass fiber and cellulosic pulps (68). Also, the strength which is imparted by a given amount of aminopolyamide—epichlorohydrin resin to handsheets of different pulps tends to be a relatively constant percentage of the dry strength, even though the absolute values of dry and wet strength vary widely. The new bond theory is supported by observations that wet and dry strength increase by approximately equal increments using acid-curing urea–formaldehyde and melamine–formaldehyde resins or using alkaline-curing aminopolyamide–epichlorohydrin resins (69–71).

Whatever its mechanism, the development of wet strength usually requires formation of a covalently bonded network of resin-to-resin or resin-to-cellulose bonds, or both. To optimize the performance of a cationic wet-strength additive, especially the aminopolyamide–epichlorohydrin type, the chemical should be added to the long fiber furnish, to minimize contact and adsorption on cellulose fines. Resin adsorbed on fines contributes much less to the paper's ultimate wet and dry strength than resin adsorbed on the long fiber portion (72). In urea–formaldehyde or melamine–formaldehyde resins, alum or acid catalyzes insolubilization of resin through methylene ether cross-links with expulsion of water. In alkaline-curing resins, epoxy or 3-hydroxyazetidinium groups cross-link with amine groups on the resin (73) or with cellulose hydroxyls and carboxyls (74). In both kinds of resins, the cross-links are difficult to hydrolyze; therefore, they impart wet strength which survives prolonged soaking. The aldehyde resins, eg, blocked aldehyde–starch and polyacrylamide–glyoxal, probably react with cellulose hydroxyls to form hemiacetal bonds which, though covalent, are hydrolyzed rapidly, resulting in the fugitive wet strength discussed previously.

2.3.6. Environmental Concerns

Concern about formaldehyde in the workplace has caused a permanent shift from UF and MF resins to polyamide– epichlorohydrin resins. UF and MF products typically contained 0.5–3.0% free formaldehyde in order to maintain stability and performance. Concern has been raised about whether a workplace hazard might occur owing to the presence of free epichlorohydrin in those neutral-to-alkaline resins produced with it. However, the residual epichlorohydrin in these resins has been well below the current reporting requirements for these materials (SARA regulations require products containing >1000 ppm (0.1%) of epichlorohydrin to be labeled), and often below detection limits (at 1 ppm by gas chromatography/mass spectrometry) (75). Concern has been raised about the presence of 1,3-dichloro-2-propanol, a hydrolysis product of epichlorohydrin, in products made with epichlorohydrin. Though not currently regulated, products have been designed to have minimal levels of 1,3-dichloropropanol (<1000 ppm) and performance levels similar to those of polyamide—epichlorohydrin resins (76–79). Obviously, the same concern could be raised about any product manufactured with epichlorohydrin, including many retention-aid polymers. However, in monitoring of workplace air, the presence of epichlorohydrin or 1,3-dichloro-2-propanol is usually not detected except in the headspace of improperly vented storage tanks (75). For air monitoring, the current detection limit is about 0.5 ppm. With formaldehyde-containing strength additives, significant levels of formaldehyde can be detected in the workplace, at both the paper mill and at subsequent converting operations when the paper is rewet and dried.

The proposed cluster rules would limit the discharge of adsorbable organic halide (AOX) from an integrated bleached pulp/paper mill (80). Though most of the AOX in mill effluent originates in the bleaching process (and some is naturally occurring in the trees prior to pulping (81)), concern has been raised about the organic chloride-containing components present in products manufactured with epichlorohydrin. Products that have been designed to contain reduced levels of 1,3-dichloro-2-propanol also have reduced levels of AOX (76–79). Additionally, the organic chloride-containing components of paper additives are most often small, highly water-soluble molecules that degrade in mill effluent treatment systems and also would not tend to bioaccumulate in fatty tissues (82).

2.4. Fillers

Opacity must be high enough in paper with print or writing on both sides of the sheet to prevent images from showing through from the back side. Newsprint typically has had sufficient opacity because the many small groundwood fibers provide much greater surface area from which light can scatter than the larger fibers in typical chemical pulps. In more permanent, higher quality papers, the chemically pulped, bleached fibers are not high in scattering power and do not produce high opacity paper, particularly when the basis weight of the paper is low, eg, $<65\ \mathrm{g/m^2}$. Opacity is increased by incorporating particulate materials or fillers into the sheet in order to increase the scattering of light which passes through the sheet (see Fillers).

Though functionally and chemically similar, fillers and pigments are distinguished from one another in that fillers are added at the wet end of the paper machine, and serve to fill the sheet; pigments are added at the size press and serve to alter the surface of the sheet. The most common fillers are mineral pigments, eg, clay, titanium dioxide [13463-67-7], calcium carbonate, silica [7631-86-9], hydrated alumina [21645-51-2], and talc [14807-96-6]. Kaolin clay [1332-58-7] is the least expensive and most widely used filler pigment in the United States (83). Methods have been devised to render almost any filler cationic, thus enhancing its retention on the fiber (84). Calcium carbonate has been limited to use in papermaking systems where the pH is neutral or slightly alkaline, because it dissolves in low pH systems. Until recently, most of the calcium carbonate that was used as filler for paper in the United States was produced by a precipitation process (PCC). Newer developments in surface-modified PCC may allow for its use in more acidic environments (85). The use of naturally occurring ground calcium carbonates (GCC) as fillers is increasing in the United States because PCC has been shown to have a more negative impact on internal sizing than does GCC (86, 87). In Europe, natural calcium carbonates are widely used because they are readily available in suitable, small-particle size and are less expensive than clay.

Overall, the use of these fillers in paper has been increasing because they are less expensive than pulp fiber. Also, as the trend toward lower basis weight continues, the use of filler increases to compensate for opacity losses. This has been especially true in newsprint, where demands on the sheet for print performance coupled with reduced basis weight has led to a significant use of filler (88, 89). As the bulk of the sheet is enhanced by filler at the expense of fiber, the loss in sheet strength has to be compensated for, mechanically or chemically. Additionally, the higher surface area of fillers can consume papermaking additives, eg, sizing and strength additives whose destination was to be the fiber, necessitating an increase in the use of these additives to achieve the targeted paper properties (87). Cationically modified fillers do not cause quite as great a deterioration of sizing chemistry (90) as do the anionic precursors.

The previously described mineral fillers function as opacifiers primarily by increasing the amount of surface area in the paper sheet and thus increasing the scattering of light. All of these fillers are characterized by refractive indexes that are similar to that of the cellulose fiber, ie, 1.53. Titanium dioxide not only increases surface area but scatters light within the particle because of its high refractive index, ie, 2.5–2.7. Unlike the other mineral pigments, titanium dioxide is considerably more expensive than the pulp fiber in the paper. Therefore, it is used in grades of paper that require high opacity and high brightness (91).

In recent years, synthetic polymeric pigments have been promoted as fillers for paper. Pigments that are based on polystyrene [9003-53-6] latexes and on highly cross-linked urea–formaldehyde resins have been evaluated for this application. These synthetic pigments are less dense than mineral fillers and could be used to produce lightweight grades of paper, but their use has been limited in the United States.

3. Functional Surface Treatments

Although many functional chemicals can be added to the wet end of the paper machine, some grades of paper require special properties that cannot be provided by the low levels of wet-end additives that are retained in the interior of the sheet of paper. Examples are high quality printing and writing paper, which require high levels of ink holdout and surface strength, and ink jet printing paper, which requires high levels of ink holdout, resistance to wicking, and resistance to color-to-color bleed. To achieve the properties required for these grades of paper, it is necessary to apply special chemicals to the surface of the preformed paper web.

3.0.1. Processes

The most common method for the application of chemicals to the surface of a paper web is by a size press. In the size press, dry paper, which usually is sized to prevent excess water and chemical penetration, is passed through a flooded nip or pond, and a solution or dispersion of the functional chemical contacts both sides of the paper. Excess liquid is squeezed out in a press and the paper is redried.

The gate-roll size press is used for the application of high solids, high viscosity compositions to the surface of the sheet (92). The material to be applied is transferred over a series of rolls, and a thin film from the applicator roll is applied to the sheet.

At high speeds, the pond of the flooded nip size press becomes turbulent. Roll maintenance is a problem with the gate-roll size press. To avoid these problems, the blade/rod metering size press was developed. Short-dwell coater heads are used to apply a precisely controlled quantity of chemicals to the size press rolls. This quantity is controlled with either a metering blade or a metering rod. Blade or rod metering eliminates the pond, and does not increase the number of rolls required for surface chemical application.

Spray applications to the surface of the sheet have been useful, especially for application of creping aids and release agents in towel and tissue mills. The spray application of functional chemicals has not been used widely. Generally, the uniformity of application is more difficult to control when functional chemicals are sprayed than when they are applied by a size press. Functional chemicals also can be applied to heavier grades of paper or paperboard at the calender stack.

3.1. Sizing

The most commonly used materials for surface sizing are starches and modified starches, including oxidized [65996-62-5], enzyme-converted [65996-64-7], hydroxyethylated [9005-27-0], and cationic starches. They are used not only for sizing, but also to improve strength, especially surface strength, and to impart smoothness. Starches may be applied to the finished sheet by any of the previously discussed methods. Often starch is used with other surface sizing agents, such as synthetic polymeric sizing agents. These combinations permit improved sizing against liquid penetrants, increased surface strength, and better finish.

Synthetic polymeric sizing agents contain hydrophobic elements and water-soluble functionalities. The two most popular classes of synthetic polymeric sizing agents are styrene–maleic anhydride copolymers (93) and polyurethane dispersions. Styrene–maleic anhydride copolymers (SMAs) use styrene as the hydrophobic element and the hydrolyzed maleic anhydride ring as the water-soluble functionality. These copolymers are extremely popular because they improve a large number of paper properties (94). These film formers improve sizing, improve printability, improve surface strength, increase paper surface coefficient of friction, and decrease paper porosity or permeability to air flow.

Polyurethane dispersions are used in specialty applications, where high levels of sizing are needed. Wax emulsions and wax–rosin emulsions also are used by themselves as surface-applied sizing agents to produce very high resistance to liquid penetration in paper and paperboard. Other products that are used as surface sizes include CMC and poly(vinyl alcohol), which provide oil- and grease-repellent coatings, improve paper strength, and decrease paper porosity.

Alkylketene–dimer emulsion sizes can be applied to the surface of paper and provide very efficient sizing. Used by themselves, these sizing agents can provide a slippery surface; consequently, they often are used in conjunction with starch or some filler which reduces slipperiness without detracting from sizing efficiency.

Fluorochemical emulsion sizing agents can be applied to the surface of paper or paperboard to provide good oil and grease repellency. If they are used with other sizing agents, eg, alkylketene dimer emulsions, both oil and grease repellency and water repellency are obtained. Fluorochemical surface treatments are used for pet-food bag paper, labels, coupons, cookie bags, candy wrappers, snack food bags, reprographic papers, and meat, fish, and poultry wrap.

3.2. Application of Dry-Strength Additives

The various water-soluble natural and synthetic polymers which are used for strength enhancement by internal addition can be applied to paper surfaces. This type of application usually is indicated when surface strength properties are more important than increased internal strength. Starches and modified starches, especially cationic starches, are used in large quantities to improve the surface strength of paper; they also improve the printing quality of the paper as a result of increased surface strength and reduced linting. The natural gums, eg, guar, locust bean, and tamarind, also can be applied to the surface of the paper to enhance strength. Likewise, various derivatives of these natural gums can be used. The acrylamide polymers normally are not used for surface applications, since they can be retained effectively during the papermaking operation. However, they can be used where primarily surface strength improvement is desired. All of these applications can be made by any of the techniques previously described.

3.3. Application of Wet-Strength Resins

Wet-strength resins seldom are applied to the surface of paper for enhancing wet strength because the commercially available, cationic wet-strength resins are retained so effectively internally. However, wet-strength resins are applied frequently to the surface of towels and tissues as creping aids.

3.3.1. Creping

The products that are used as internally added creping aids can be applied to the surface of paper, usually by spraying an aqueous solution or emulsion in front of the Yankee dryer. One of the most commonly used resins for this purpose is an aminopolyamide–epichlorohydrin resin. Such resins yield coatings on the dryer with the required degree of adhesion for optimum creping. If the internally added wet-strength resin yields excessive adhesion to the dryer, a release agent, eg, a silicone–oil emulsion, can be sprayed on the sheet. Application of creping aids to the sheet in front of the dryer permits rapid manipulation of the degree of adhesion by varying the ratio of adhesive to release agent.

3.3.2. Curl Control

Many grades of paper tend to curl, especially as humidity varies, because of the stresses produced during the drying process. This is especially troublesome when only one side of the paper receives a surface treatment. Judicious application of water to the opposite side of the dry sheet followed by redrying may correct the curling. Water may be applied by surface application at the size press, water box, or calender stack or it may be sprayed on. Small amounts of water can be applied to the paper surface as a foam with excellent results.

3.4. Pigmented Coatings

Conventional paper has a surface that is not well suited to high speed printing processes, principally because the surface is rough; thus, contact of the surface with printing elements is poor. Furthermore, in quality printing, a high level of gloss in both the printed areas and in the substrate often is desirable. High levels of gloss cannot be attained with the rough surface of conventional paper. For these reasons, a large volume of paper is coated in order to improve printability. The main function of the coating is to provide a smooth surface for printing. Other properties that are important to the coating are receptivity to inks and sufficient surface strength to withstand the forces of the printing process on the coated paper.

Paper coatings are applied as coating colors, which are aqueous slurries containing 35–65 wt % solids. There are three main components of the solids; pigments, binders, and minor additives. The pigment is the primary component of a paper coating and consists of small, white, particulate material. Pigments usually are minerals, eg, clay, calcium carbonate, or titanium dioxide. The packed pigment particles fill pitted areas of the rough paper surface, thereby providing a suitable surface for printing. Binders are the resins or polymers that function as the glue that binds the pigment particles to each other and to the paper substrate. The level of binder is low in a paper coating, typically 5–30 parts by weight per 100 parts of pigment. This low level of binder distinguishes paper coatings from paints, which are pigment-filled polymer films. Minor additives are used to modify the properties of the coating color, primarily before and during the coating operation.

3.4.1. Pigments

The pigments which are used in paper coatings are similar to the materials that are used as fillers (83, 88). Kaolin clay is the largest-volume pigment for this application. The clay that is used in coatings is of better quality and is slightly more expensive than that used as a filler. Coating clays are higher in brightness and have a smaller particle-size distribution than the filler clays. Structured kaolin pigments (95, 96), in which the base clay is aggregated or flocculated rather than calcined, provide enhanced opacity and oil absorption.

Finely ground calcium carbonate is second in volume to kaolin clay as a paper-coating pigment. Titanium dioxide is used in coated grades of paper requiring high levels of brightness and opacity. Preblending calcium carbonate with titanium dioxide produces a pigment that scatters light almost as well as titanium dioxide alone, but at a lower cost (97). Plastic pigments that are based on polystyrene are used in combination with mineral pigments to improve the gloss of coated paper. The use of hollow acrylate polymer latex particles in coating formulations has shown promise for the gloss-enhancement of paper and paperboard (98).

Satin white [12004-14-7] is another paper-coating pigment and is prepared by the reaction of calcium hydroxide with alum. In combination with other mineral pigments, satin white produces coatings with improved ink receptivity, gloss, smoothness, and brightness. Satin white usually is used as <25 wt% of the pigment system, because it causes rheological problems at higher levels. Most satin white is produced by paper companies for their own use.

3.4.2. Binders

Paper-coating binders are either polymers derived from natural sources or synthetic polymers. The largest volume, naturally derived binder is starch (qv) (99). Starch is provided in derivatized form or unmodified form; pearl corn starch is used predominantly for the latter. Unmodified starch is solubilized by thermal conversion or enzyme conversion. The most common derivatized products are acetylated [9045-28-7], oxidized, and hydroxyethylated starches.

The other main natural binder is protein that is prepared by extraction from soy meal (100). Casein [9000-71-0], once a large-volume paper-coating binder, has markedly declined in use because of its high price and susceptibility to microbial attack.

Almost all synthetic binders are prepared by an emulsion polymerization process and are supplied as latexes which consist of 48–52 wt % polymer dispersed in water (101). The largest-volume binder is styrene–butadiene copolymer [9003-55-8] (SBR) latex. Most SBR latexes are carboxylated, ie, they contain copolymerized acidic monomers. Other latex binders are based on poly(vinyl acetate) [9003-20-7] and on polymers of acrylate esters. Poly(vinyl alcohol) is a water-soluble, synthetic binder which is prepared by the hydrolysis of poly(vinyl acetate) (see Latex technology; Vinyl polymers).

3.4.3. Other

A large variety of additives are used in paper-coating colors primarily to modify the physical properties of the colors (102). At high solids concentrations in water, mineral pigment particles tend to associate and form viscous pastes. Dispersants (qv) are used to prevent this and to provide low viscosity slurries. Common dispersants include polyphosphates and sodium polyacrylate [9003-04-7]. Various water-soluble polymers are added to coating colors and act as water-retention agents and as rheology modifiers.

Hydrophilic polymers function as water-retention aids by preventing premature dewatering of the coating color after it has been applied to the paper but before the paper has been dried. Water-soluble polymers, eg, CMC, hydroxyethylcellulose [9004-62-0], guar gum and derivatives, and sodium alginate [9005-38-3], improve the rheological properties of coating colors and help keep the colors on the surface of the paper rather than striking into the sheet. Lubricants are added to coating colors to improve the lubricity of the wet coating color and to improve the properties of the dried coating. In particular, lubricants prevent sticking of the dry coatings to surfaces of calenders. Common lubricants include calcium stearate [1592-23-0], fatty acid esters, sulfonated oils, and wax emulsions.

4. Synthetic Fibers

A variety of wet-laid felts and nonwoven fabrics are produced on Fourdrinier-type paper machines (103, 104) (see Nonwoven fabrics). Noncellulosic materials may be included as part or all of the fiber furnish; latexes, water-soluble polymers, or other adhesives are used as bonding agents. Synthetic fibers can make paper highly resistant to wetting; chemical attack; mechanical wear, eg, folding; weathering; and biological degradation. Synthetic fiber-containing papers are used as backings for carpets and vinyl floor coverings, industrial filters, disposable bed linens and hospital garments, heavy-duty wiping materials, tea bags, tissues, labels, and embossable wall papers.

Water-laid cellulose papers contain strong interfiber bonds which result from overlap, interpenetration, and consolidation of swollen fiber surfaces. The main synthetic fibers swell little, if at all, in water, and require special bonding techniques whether they are water-laid or air-laid. Bonding techniques include swelling of fiber crossover points by organic solvents or by salt solutions, which become concentrated during drying, and controlled melt bonding. Bonding with fibrids depends on fusion and entanglement of small, branched, fibrillated fibers (105, 106). Nylon and polyester fibers improve wet strength, tear strength, and fold resistance of papers (107).

Heavy-duty wiping materials and some disposable garments are made from nonwoven cellulose mats which are reinforced with a synthetic fiber, eg, nylon scrim network; the spacing of the synthetic threads is 0.5–1.0 cm (108).

Asbestos [1332-21-4] fiber traditionally is used with a latex binder in backings for roll-vinyl floor coverings, but the long-term health hazards which asbestos (qv) presents have initiated a search for substitutes, eg, glass wool, rock wool, polyolefin fibers, and cellulose. Polyolefin fibers have been investigated extensively as substitutes for cellulose and asbestos fibers in papermaking because of the formers' good optical properties, low density, thermoplasticity, inertness, and machine productivity. Because they float on water and have hydrophobic surfaces, polyolefin fibers require chemical or mechanical pretreatments so that they can be dispersed in water. Although polyolefin fibers cost more than cellulose, they are cost-effective because their low density and high surface area:weight ratio provides comparable print quality and opacity at lower sheet weights than do all-cellulose papers. Polyolefin–cellulose composites also are used in nonasbestos flooring felts, wallpapers, filter media, labels, embossable papers, and other nonwoven fabrics that are made on paper machines. Use of synthetic fibers in paper has been reviewed (103, 104).

BIBLIOGRAPHY

"Papermaking Additives" in *ECT* 3rd ed., Vol. 16, pp. 803–825, by S. T. Putnam, H. H. Espy, and G. G. Spence, Hercules Inc.

Cited Publications

1. H. K. Berry, *Papermaker* (2), 35–37 (1994).
2. B. A. Egan and R. Dickinson, *Pulp Paper*, **64**(6), 110–113 (1990).
3. *Title 21 Code of Federal Regulations*, Subchapter B, Part 176, Sections 170, 180, U.S. Government Printing Office, Washington, D.C., Apr. 1, 1992.
4. D. E. Boardman, *Tappi* **76**(12), 148–152 (1993).
5. D. Guest, *Paper Technol.* **31**(6), 40–43 (1990).
6. *Pulp and Paper 1993 Buyers Guide Issue*, Miller Freeman, Inc., San Francisco, Calif., 1993, 93–111.
7. R. M. Husband, ed., *Survey of Paper Additives*, 2nd ed., H&H Consulting Group, Trunball, Conn., 1989.
8. L. H. Allen and I. M. Yaraskavitch, *Tappi* **74**(7), 79–84 (1991).
9. J. E. Lukins, *Pulp Paper* **67**(4), 69–71 (1993).
10. P. Arvela, J. W. Swanson, and R. A. Stratton, *Tappi* **58**(11), 86 (1975).
11. W. E. Frankle and J. L. Sheridan, *Tappi* **59**(2), 84 (1976).
12. K. W. Britt, *Tappi* **56**(3), 83 (1973).
13. K. W. Britt, *Tappi* **56**(10), 46 (1973).
14. U.S. Pat. 5,185,062 (Feb. 9, 1993), A. J. Begala (to Nalco Chemical Co.).
15. U.S. Pat. 5,266,164 (Nov. 30, 1993), R. W. Novak and T. C. Fallon (to Nalco Chemical Co.).
16. L. Wagberg, X. P. Zhao, I. Fineman, and F. N. Li, *Tappi* **73**(4), 177–182 (1990).
17. B. Carre, *Nordic Pulp Paper Res. J.* **8**(1), 21–26 (Apr. 1993).
18. R. I. S. Gill, "Developments in Retention Aid Technology," *Paper Technol.*, 6–11 (Aug. 1991).
19. P. Kubelka and F. Munk, *Z. Tech. Phys.* **12**, 593 (1931).
20. P. Kubelka, *J. Opt. Soc. Am.* **39**(5), 448 (1948).
21. J. A. Van den Akker, *Tappi* **32**(11), 498 (1949).
22. F. A. Steele, *Paper Trade J.* **100**(12), 37 (1935).
23. K. W. Britt and J. E. Unbehend, *Tappi* **59**(2), 67 (1976).
24. P. F. W. Lee and T. Lindstrom, *Nordic Pulp Paper Res. J.* **4**(2), 61–70 (July 1989).
25. U.S. Pat. 5,185,061 (Feb. 9, 1993), P. Lowry and D. Farrar (to Allied Colloids Ltd.).
26. K. W. Britt and J. E. Unbehend, *Tappi Papermakers Conference Proceedings 1980*, Tappi Press, Atlanta, Ga., 1980, pp. 5.
27. L. F. Twoomey, *Tappi* **70**(9), 87–90 (1987).

28. R. H. Voss, C. E. Luthe, B. I. Fleming, R. M. Berry, and L. H. Allen, “Some New Insights into the Origins of Dioxins Formed During Chemical Pulp Bleaching,” paper presented at the *CPPA Environment Conference 1988*, Vancouver, B.C., Canada, Oct. 25–26, 1988.
29. *Questions and Answers: Water-Based Antifoams*, Nalco Chemical Co., Oak Brook, Ill., 1983.
30. M. Laleg and I. I. Pikulik, *Nordic Pulp Paper Res. J.* **6**(3), 99–109 (Oct. 1991).
31. L. R. Peel, *Paper Technol.* 20–23 (Dec. 1989).
32. M. Laleg and I. I. Pikulik, *J. Pulp Paper Sci.* **17**(6), J206–J216 (1991).
33. S. D. Goldstein, *Tappi* **75**(7), 85–92 (1992).
34. L. H. Allen and C. L. Lapointe, *Nordic Pulp Paper Res. J.* **4**(2), 94–98 (July 1989).
35. T. Hassler, *Tappi* **71**(6), 195–201 (1988).
36. D. S. Rende, *Pima* **76**(2), 32–33 (1994).
37. U.S. Pat. 5,139,616 (Aug. 18, 1992), T-F. Ling (to Betz PaperChem, Inc.).
38. J. A. Koncel, *Amer. Papermaker* **54**(2), 50–51 (1991).
39. J. A. Glazer, *Tappi* **74**(7), 72–74 (1991).
40. A. S. Nigrelli, *Pulp Paper* **64**(11), 68–72 (1990).
41. J. P. Oliver, *Tappi* **63**(12), 91–95 (1980).
42. R. W. Davison, *Tappi* **58**(3), 48 (1975).
43. E. W. Washburn, *Phys. Rev.* **17**, 273 (1921).
44. J. Marton, *Nordic Pulp Paper Res. J.* **4**(2), 77–80 (July 1989).
45. J. Marton and F. L. Kurrle, *J. Pulp Paper Sci.* **13**(1), J5–J9 (June 1987).
46. L. J. Stryker, B. D. Thomas, Jr., and E. Matijevic, *J. Colloid Interface Sci.* **43**(2), 319–329 (May 1973).
47. J. Marton and F. L. Kurrle, *Canad. J. Pulp Paper Sci.* **13**(1) (1987).
48. B. Wortley, *Pulp Paper*, **64**(11), 131–133 (1990).
49. M. C. Peck and M. A. Markillie, *Tappi Papermakers Conference Proceedings 1994*, Tappi Press, Atlanta, Ga., 1994, p. 165–168.
50. J. Marton, *Tappi* **73**(11), 139–143 (1990).
51. B. W. Crouse and D. G. Wimer, *Tappi* **74**(7), 152–159 (1991).
52. W. J. Andounian, *Pima* **75**(7), 48–49 (1993).
53. G. B. Kelly, Jr., *Alkaline Paper Advoc.* **2**(1), 9–10 (Apr. 1989).
54. J. Marton and D. D. Jarrell, *Sizing Short Course 1987*, Tappi Press, Atlanta, Ga., 53–62.
55. A. R. Colasurdo and I. Thorn, *Tappi* **75**(9), 143–149 (1992).
56. R. W. Novak and D. S. Rende, *Tappi* **76**(8), 117–120 (1993).
57. J. Marton, *Tappi* **74**(8), 187–191 (1991).
58. *TAPPI Test Methods, 1992–1993*, Tappi Press, Atlanta, Ga., 1992.
59. C. E. Farley, *Tappi Papermakers Conference Proceedings 1986*, Tappi Press, Atlanta, Ga., 147–150.
60. F. M. K. Werdouschegg, in W. F. Reynolds, ed., *Dry Strength Additives*, Tappi Press, Atlanta, Ga., 1980, 67–93.
61. M. Laleg and I. I. Pikulik, *J. Pulp Paper Sci.* **19**(6), J248–J255 (Nov. 1993).
62. W. F. Reynolds, in Ref. 60, 125–148.
63. U.S. Pat. 3,049,469 (Aug. 14, 1962), R. W. Davison (to Hercules Inc.).
64. U.S. Pat. 3,332,834 (July 25, 1967), W. F. Reynolds (to American Cyanamid Co.).
65. H. J. Leech, *Tappi* **37**(8), 343 (1967).
66. *Tappi Wet and Dry Strength Short Course 1988*, Tappi Press, Atlanta, Ga., 1988.
67. W. Kamutzki, *Polym. Paint Colour J. (Suppl.)*, 108–114 (1989).
68. H. L. Marder, S. E. Church, and V. Stannett, *Tappi* **40**(10), 829 (1957).
69. A. Jurecic, C. M. Hou, K. Sarkanen, C. P. Donofrio, and V. Stannett, *Tappi* **43**(10), 861 (1960).
70. D. J. Salley and A. F. Blockman, *Tech. Assoc. Pap.* **30**, 223 (1947); *Pap. Trade J.* **125**(1), 35 (1947).
71. A. Jurecic, T. Lindh, S. E. Church, and V. Stannett, *Tappi* **41**(9), 465 (1958).
72. R. A. Stratton, *Nordic Pulp Paper Res. J.* **4**(2), 104–112 (July 1989).
73. D. I. Devore and S. A. Fischer, *Tappi* **76**(8), 121–128 (1993).
74. H. H. Espy and T. W. Rave, *Tappi* **71**(5), 133–137 (1988).
75. M. A. Dulany, *technical data*, Georgia-Pacific Paper Chemicals Laboratory, Decatur, Ga., 1992–1994.
76. D. I. Devore, N. S. Clungeon, and S. A. Fischer, *Tappi* **74**(12), 135–141 (1991).

77. U.S. Pat. 5,019,606 (May 28, 1991), M. Marten and W. Kamutzki (to Hoechst, AG).
78. U.S. Pat. 5,189,142 (Feb. 23, 1993), D. I. Devore and S. A. Fischer (to Henkel Corp.).
79. U.S. Pat. 5,239,047 (Aug. 24, 1993), D. I. Devore and S. A. Fischer (to Henkel Corp.).
80. A. Rooks, *Pima* **75**(11), 34–40 (1993).
81. O. Dahlman and co-workers, *Environ. Sci. Technol.* **27**(8), 1616–1620 (1993).
82. G. R. Craig, P. L. Orr, J. L. Robertson, and W. M. Vrooman, *Pulp Paper Can.* **91**(9), 39–45 (1990).
83. R. W. Hagemeyer, ed., *Pigments for Paper*, Tappi Press, Atlanta, Ga., 1984.
84. U.S. Pat. 5,169,441 (Dec. 8, 1992), R. V. Lauzon (to Hercules Inc.).
85. M. Tokarz, R. Sikkar, and S. Jaras, *Nordic Pulp Paper Res. J.* **5**(2), 88–92 (July 1990).
86. M. C. Peck, *technical data*, Georgia-Pacific Paper Chemicals Laboratory, Decatur, Ga., 1991–1993.
87. J. Marton, in *Papermaking Raw Materials*, Vol. **2**, Mechanical Engineering Publications Ltd., London, 785–813 (1985).
88. A. Rook, *Pima* **75**(7), 39–45 (1993).
89. C. A. Skrocki and C. D. Richardson, *Pulp Paper*, **64**(2), 65–69 (1990).
90. U.S. Pat. 5,147,507 (Sept. 15, 1992), R. A. Gill (to Pfizer, Inc.).
91. B. Siffert and J-M. Metzger, *Coll. Surf.* **53**, 79–99 (1991).
92. R. J. Alheid, *Tappi Papermakers Conference Proceedings 1978*, Atlanta, Ga., p. 83.
93. G. L. Batten, Jr., *Tappi Papermakers Conference Proceedings 1992*, Atlanta, Ga., 159–168.
94. T. W. Tompkins, in Ref. 93, 169–174.
95. R. W. Dahlquist, R. E. Hardy, and L. J. Welch, *Pulp Paper* **63**(11), 90–93 (1989).
96. T. L. Kellogg and R. E. Hardy, *Pulp Paper*, **67**(5), 71–74 (1993).
97. W. E. Scott, *Am. Papermaker* **50**(5), 12–14 (1987).
98. U.S. Pat. 5,157,084 (Oct. 20, 1992), D. I. Lee, M. R. Mulders, D. J. Nicholson, and A. N. Leadbetter (to The Dow Chemical Co.).
99. *Tappi Monogr. Ser.* **17** (1957).
100. *Tappi Monogr. Ser.* **36** (1975).
101. *Tappi Monogr. Ser.* **37** (1975).
102. C. G. Landes and L. Knoll, eds., *Paper Coatings Additives*, Tappi Press, Atlanta, Ga., 1978.
103. O. A. Battista, ed., *Synthetic Fibers in Papermaking*, Wiley-Interscience, New York, 1964.
104. R. W. Moncrieff, *Man-Made Fibres*, Halstead Press, a division of John Wiley & Sons, Inc., New York, 1975.
105. R. A. A. Hentschel, *Tappi* **42**(12), 979 (1959).
106. L. A. Auspos and E. B. Winn, *Tappi* **45**(9), 741 (1962).
107. G. L. McLeod, *Tappi* **41**(8), 430 (1958).
108. U.S. Pat. 3,616,133 (Oct. 26, 1971), G. D. Thomas (to Kimberly-Clark Corp.).

MARGARET A. DULANY
GEORGE L. BATTEN JR.
MICHAEL C. PECK
CHARLES E. FARLEY
Georgia-Pacific Resins, Inc

Related Articles

Flocculating agents; Industrial antimicrobial agents; Paper