

Chemical Additives

M A Hubbe, North Carolina State University, Raleigh, NC, USA

© 2004, Elsevier Ltd. All Rights Reserved.

Introduction

Chemical additives can be critical to the economic viability of paper machines. Relative to fibers (*see Pulp*: Fiber Resources), other materials are present in paper and paperboard at much lower levels. However, additives allow papermakers to differentiate their products to meet the differing needs of customers. They also use additives to make their operations more efficient. This article considers the most widely used papermaking additives, focusing on their composition, their modes of preparation and use, and their impacts on either product attributes or process efficiency. The fact that relatively small amounts of additives can make huge differences makes this a fascinating field of work and study.

Why use Additives During Paper Manufacture?

If you tour a typical papermaking operation you cannot help being struck by the capital-intensive nature of this business. To thrive in a capital-intensive industry it is essential to run the capital equipment as effectively as possible. In contrast, from the viewpoint of the papermaker, chemical additives represent an operating cost, not a capital cost. Those responsible for papermaking operations can decide on a month-to-month basis whether a given additive makes a big enough difference to justify its continued use.

There are two main classes of chemical additives applied in paper machine systems, and each of these involves different motivations concerning its use. The term 'functional additives' will be used here when referring to additives that change paper properties so that they better meet customer needs. A universal customer need is to cut costs; for this reason it makes sense to consider mineral fillers among the other functional additives to be described in this article. Other functional additives include materials to make paper stronger (dry-strength and wet-strength agents), materials to make paper resist water and other fluids (sizing agents), and materials to change the shade or brightness of paper (dyes, pigments, and fluorescent whiteners).

The term 'process additives' will be used here for materials that mainly affect the way the paper

machine operates. Factors that determine the overall efficiency of papermaking operations include the speed of the paper machine. Papermaking involves rapid removal of huge amounts of water from fiber slurries (*see Papermaking*: Overview). Sometimes removal of water is the production-limiting step. So papermakers treat the furnish with drainage aids, an example of process additives, to allow water to be removed more easily. Another factor governing efficiency is the percentage of time during which the paper machine is successfully making product, i.e., up-time. A key enemy of up-time is the tendency of various materials to deposit on to papermaking equipment. Deposited material often becomes entrained again in the process, leading to spots or holes in the paper, web breaks, and costly downtime. Deposits in press felts, often called 'felt filling,' can cause moisture streaks or just make it necessary to slow down the machine. Chemicals used to fight deposits, as well as the related issues of slime and foam, are further examples of process additives.

Functional Additives for Papermaking

Mineral Fillers

Mineral fillers rank first among papermaking additives in terms of the amounts used. Many paper and paperboard grades contain little or no filler, while printing papers commonly contain up to 25% filler, by mass.

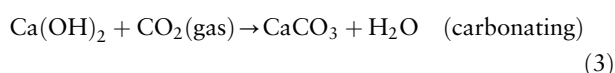
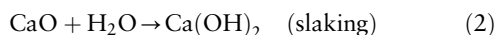
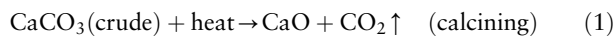
Though the word 'filler' would seem to suggest otherwise, there are numerous reasons to add mineral products to paper. These reasons include cost reduction, enhancement of opacity or brightness (*see Pulp*: Physical Properties), and enhanced smoothness of paper after calendering (*see Papermaking*: Overview). The minerals do not 'fill' all of the space between fibers in a sheet of paper. In fact, the use of fillers does not necessarily decrease the volumetric proportion of air space. Depending on their detailed locations, filler particles may act as spacers between fibers in the sheet, increasing its thickness or 'caliper' under given processing conditions or at a given target of paper smoothness.

The most widely used mineral products in paper manufacture, including those used in coating of paper (*see Papermaking*: Coating), are calcium carbonate, kaolin clay, titanium dioxide, and talc. The most common particle size range of fillers is between about 0.5 and 4.0 μm . An exception is titanium dioxide (TiO_2), the particles of which typically have diameters in the range 0.2–0.3 μm . Because TiO_2 is mainly used to improve paper's

opacity, its size is dictated by the need to maximize the scattering of light.

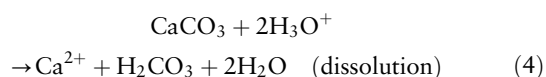
Calcium carbonate Presently in the USA calcium carbonate (CaCO_3) is the major mineral additive for papermaking. The main varieties of CaCO_3 filler are as shown in Table 1.

The process for preparing precipitated CaCO_3 (PCC) can be represented by the following formulae:



Because the mass of CaO (lime) is only 56% of the mass of the corresponding CaCO_3 , and in order to minimize transportation costs, it is common to carry out reaction (1) near to the mine, and to carry out reactions (2) and (3) adjacent to a paper mill. The precipitation process allows control of the particle sizes and shapes in ways that favor paper grades with differing requirements for brightness, opacity, smoothness, and strength.

The emergence of CaCO_3 as the major papermaking filler during the 1980s and 1990s profoundly affected operating conditions in paper mills, including the pH values and the kinds of sizing agents employed. The following reactions take place when CaCO_3 is placed in acidic solution, i.e., water with a pH lower than about 6:



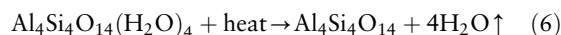
Due to these reactions, the use of CaCO_3 typically implies neutral or weakly alkaline conditions during the manufacturing process, e.g., $6 < \text{pH} < 9$.

Kaolin clay Clay remains the most used mineral product for paper coatings (see **Papermaking: Coat-**

ing), but by the 1990s it was second to CaCO_3 with respect to use as a filler. Kaolinite is a hydrous aluminum silicate, $\text{Al}_4\text{Si}_4\text{O}_{14}(\text{H}_2\text{O})_4$. Kaolin deposits in Georgia and South Carolina, having relatively narrow particle size distributions, were laid down by meltwaters from glaciers. The meltwaters slowed down when they entered the prehistoric ocean, allowing the particles to settle. After scooping the clay with a crane, it is commonly mixed with water under severe conditions of agitation in a process called 'blunging.' The clay particles in this initial mixture typically consist of 'bookettes' of clay platelets.

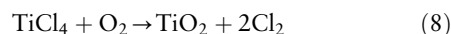
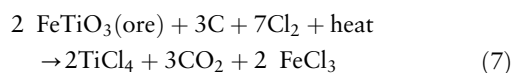
Two processes to modify clay for papermaking use are delamination and calcination. Delamination involves repeated overturning of a mixture of the clay bookettes and porcelain-grinding medium. The resulting shearing separates the clay into platelets. Papermakers favor delaminated clay when they want to decrease paper's air permeability, or when they want to improve brightness and opacity relative to conventional filler clay.

Calcined clay gets its name from the fact that the following reaction is carried out in the same kind of equipment that has been used to convert CaCO_3 to lime (see eqn [1]):



Calcination of clay fuses platelets together, and this has been found to be advantageous for bulking and optical properties of paper.

Titanium dioxide Papermakers use TiO_2 when high levels of opacity are needed, or when the market demands lighter-weight paper grades that match opacity levels of higher-weight samples. The major synthetic route for TiO_2 pigment is the so-called 'chloride' process, as follows:



A so-called 'sulfate' process is also used. By varying the manufacturing conditions it is possible to obtain TiO_2 in two crystal forms, rutile and anatase. Both mineral forms have high refractive indices, 2.7 and 2.5, respectively. By contrast, fibers, calcium carbonate, and kaolin all have refractive indices in the range of 1.5–1.6. The much higher refractive index of TiO_2 helps to explain its much greater ability to scatter light.

Table 1 Calcium carbonate filler types

	Crystal type	Shape
Precipitated calcium carbonate (PCC)		
Scalenohedral	Calcite	Rosette
Rhombohedral	Calcite	Blocky
Acicular	Aragonite	Needles
Ground limestone	Calcite	Irregular
Ground chalk	Calcite	Shell-like

Talc The most important characteristics of talc are its oil-loving surface, its platy shape, and its low hardness (1 on the Mohs scale). The low hardness makes it practical for filled paper with talc having large particles, e.g., in the range 3–10 μm . However, a more common application of talc is to control deposits of wood pitch in paper mills using mechanical pulp (see **Pulping: Mechanical Pulping**). Such applications require the use of finely divided talc, providing a high surface area of oil-loving material. The fine talc is also used to detackify sticky materials present in many recycled furnishes (see **Packaging, Recycling and Printing: Paper Recycling Science and Technology**).

Other fillers Aluminum trihydrate (ATH), having the composition $\text{Al}(\text{OH})_3$, has high brightness, and it also acts as a flame-retardant when used at high levels. Gypsum, having a composition of calcium sulfate dihydrate, is also bright and inexpensive. Due to the high solubility of gypsum, some of it is dissolved in the process water during paper manufacture. Precipitated amorphous silicas, silica aluminates, and related products are used for specialty printing applications. These noncrystalline mineral products, having high specific surface areas, can help to hold fluid inks near to the surface of paper.

Dry-Strength Agents

Papermakers add water-loving polymers both at the wet end and at the size press to increase dry strength. Reasons for using a dry-strength additive usually go beyond just meeting specified strength requirements. For instance, a dry-strength agent can compensate for the tendency of fillers to interfere with interfiber bonding. A dry-strength additive can also compensate for low-quality fiber, including recycled kraft fibers that have lost some of their bonding ability. Though it is possible to increase strength by refining (see **Papermaking: Overview**), excessive refining hurts drainage of the paper web.

Starch products are by far the most important dry-strength agents presently used in the USA. At the wet end it is most common to use cationic derivatives of corn, waxy maize (a specialty corn variety), or potato starches. Wet-end starches are carefully handled to avoid lowering their molecular mass. The most popular cationic starches contain approximately 0.2–0.3% nitrogen, in the form of quaternary ammonium salt groups. One of the reactions used by suppliers of cationic starch products is shown in **Figure 1**.

Most wet-end starches require cooking (sometimes called ‘pasting’) at the mill site. In batch operations

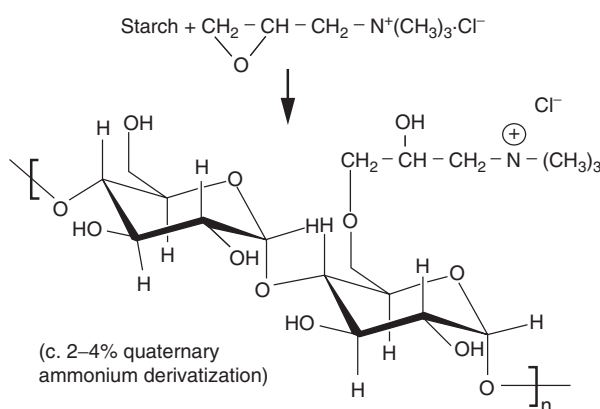


Figure 1 Synthesis of cationic starch.

the dispersed starch granules are heated at ambient pressure to just below the boiling point of water and agitated for about 20 min, at which time the granules have completed their swelling, rupture, and liberation of starch molecules. Starch can also be continuously ‘jet-cooked’ at higher temperature and elevated pressure. The combination of relatively high molecular mass and weak cationic charge makes it possible to adsorb at least 1% cationic starch, by mass, on to the fiber surfaces before formation of the sheet.

Other dry-strength additives include cationic guar gum, copolymers of acrylamide, and also various anionic polymer products such as carboxymethyl cellulose (CMC). Since fibers used for papermaking typically have a weak negative surface charge, anionic polymers added at the wet end are used in sequence with cationic additives.

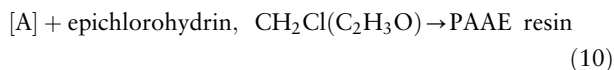
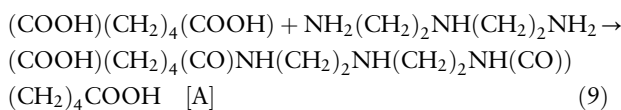
Size-press addition of dry-strength agents offers the papermaker some freedom and also some more constraints. Freedom is provided by the fact that nearly 100% of material added to paper’s surface becomes part of the product; this means that size press starches do not have to be cationic. But there is an added constraint relative to viscosity. Starch products to be used at the size press typically have to be reduced in molecular mass by treatment with a strong oxidizing agent or with an enzyme. Though the molecular mass reduction renders the starch less effective for strength, it is a necessary compromise to avoid nip rejection and other problems with size-press operations. It is common for the starch to be spread on to the surface of the paper or paperboard as a dilute solution of, say, 10% solids. Starch derivatives commonly used at the size press include unmodified starch, oxidized starch, hydroxyethylated starch, and cationic starch. In addition to starch, papermakers also use polyvinyl alcohol,

carboxymethylcellulose (CMC), alginates, and copolymers such as styrenemaleic anhydride (SMA) to enhance the surface strength of paper.

Wet-Strength Agents

Polyamidoamine-epichlorohydrin (PAAE) copolymers are widely used in the USA to help maintain the strength of paper products even after they have become thoroughly wetted. Major applications include currency, paper bags, and paper towels.

Most materials that act as wet-strength agents are polymeric, and they contain some kind of reactive group capable of cross-linking the resin during drying of the paper. PAAE is basically formed as follows:



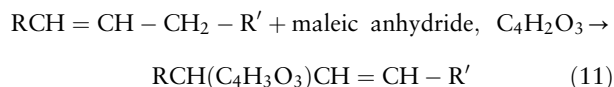
The PAAE resin has a positive charge in solution due to residual amine groups and cross-linkable azetidinium groups formed by the reaction with epichlorohydrin.

Other important wet-strength resins include glyoxylated polyacrylamide (GlyPAM) and traditional formaldehyde-based resins. GlyPAM is used in cases where a temporary wet-strength effect is desired, e.g., flushable products. Phenol formaldehyde (PF) and melamine formaldehyde (MF) resins offer many advantages, but their usage has decreased due to regulation of formaldehyde levels.

Internal Sizing Agents

The purpose of internal sizing agents, which are added at the wet end of a paper machine, is to inhibit wetting, spreading, or penetration of fluids on to and into the paper. The three major internal sizing agents are alkenylsuccinic anhydride (ASA), alkylketene dimer (AKD), and rosin products.

Alkenylsuccinic anhydride ASA is formed as follows, by the reaction between maleic acid and monounsaturated mineral oil from the distillation and cracking of petroleum:



where $\text{R} = \text{CH}_3(\text{CH}_2)_m$, $\text{R}' = \text{CH}_3(\text{CH}_2)_m$, and

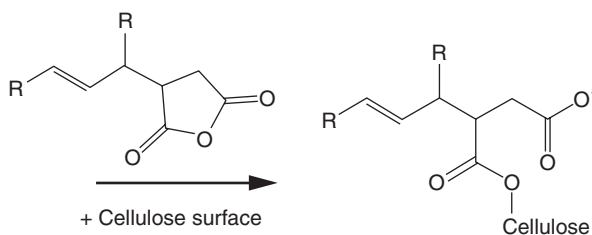
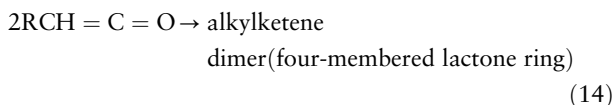
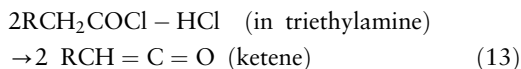
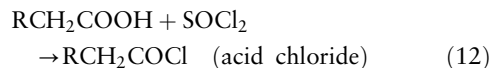


Figure 2 Reaction of alkenylsuccinic anhydride size with a fiber surface.

$(n + m) = 13, 15, 17$, or 19 . ASA oil needs to be emulsified before its addition at the wet end. Due to ASA's reactivity with water, the emulsification is carried out immediately before use, next to the paper machine. Cationic starch or a moderate-mass acrylamide copolymer can be used to stabilize the droplets of ASA that are formed by application of hydrodynamic shear. Sizing with ASA is generally understood to involve the formation of ester bonds as shown in Figure 2 during the drying process.

Alkylketene dimer AKD products are formed by reactions of fatty acids, as follows:



where $\text{R} = \text{CH}_3(\text{CH}_2)_n$, and n is an even number between about 14 and 22.

Usually the AKD is emulsified by the chemical supplier and delivered to the papermaker as a ready-to-use dispersion. Stabilizers may include either cationic starch or various synthetic cationic polymers. Though the lower reactivity of AKD relative to ASA can make it easier to apply, it is more difficult to cure. For the curing of AKD it has been proposed by many authors that the ketene dimer's lactone ring opens to form a beta-keto ester with hydroxyl groups on the fiber surface. There has been continued discussion about whether esterification occurs extensively under typical drying conditions. Other factors that may contribute to sizing by AKD include the water-hating nature of the unreacted AKD itself, and its tendency to form insoluble condensation products on heating.

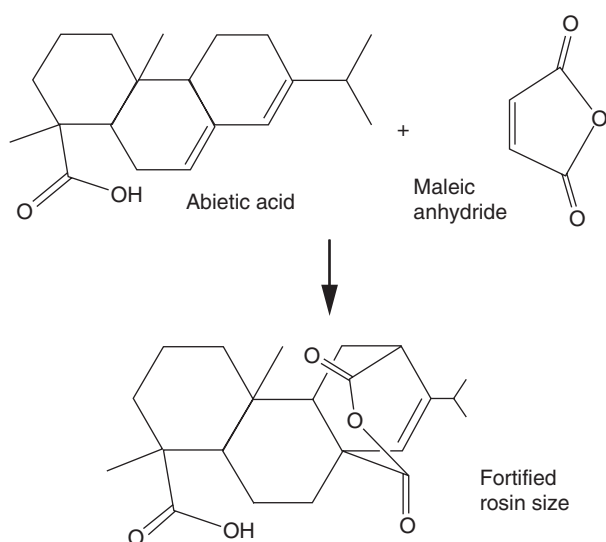


Figure 3 Fortification of rosin size molecule.

Rosin size products Crude rosin is most often obtained as a byproduct of kraft pulping (*see Pulping: Chemical Pulping*). The reaction shown in **Figure 3**, called ‘fortification,’ is carried out before the rosin is used for papermaking. Fortification tends to make rosin formulations easier to handle, less likely to crystallize during storage, and better able to react with aluminum compounds for retention and curing reactions.

Two main types of rosin size formulations are commonly used in the USA. The key difference involves the form of the carboxylic groups. In the case of emulsion-type rosin products, only enough base is added to convert a minor portion of the rosin to its salt form (saponification). The emulsion is stabilized by a cationic polymer or protein, much like the case of ASA, already described. Emulsion-type rosin products benefit from use of a retention aid to attach the particles to fiber surfaces in the wet end. During drying the rosin becomes distributed by vapor transport and a limited degree of spreading of rosin droplets on fiber surfaces. Aluminum byproducts at the paper surface can then bind the rosin. When using rosin emulsion products it is customary to use a reverse order of addition in which the aluminum compound, usually aluminum sulfate or alum, is added first, followed by the size.

Liquid rosin and traditional paste-type rosin soap products have high proportions of saponified, negatively charged carboxylate groups. This fact renders these products dispersible as micelles and monomeric ions in the water. The essential reaction for sizing takes place in the fiber slurry between rosin and a soluble aluminum or iron compound. Though papermakers often use the reverse order of addition

when adding rosin soap products in the presence of hard water, the traditional approach is to ‘set’ the size by adding the alum after the size has been mixed with the furnish.

Colorants and Fluorescent Whitening Agents

With the exception of carbon black, which is polymeric, most colorants used for paper are monomeric organic chemicals. They derive their ability to adsorb light from multiple conjugation, i.e., extensive alternation of single and double covalent bonds.

The most widely used class of papermaking dye has the color index designation of ‘direct.’ Direct dye molecules contain negatively charged sulfonate groups. The molecules are relatively big and planar, attributes that help them to be retained on fiber surfaces even without the use of a fixative chemical. When papermakers want even higher retention of dye it is possible to use another class of dye, the cationic direct dyes. However, very high affinity is not always an advantage. To avoid an unintentional speckled appearance of the paper, cationic direct dyes need to be diluted and added at a point where there is good agitation. A class of dyes called basic dyes is widely used for yellow pages and other dyed products made from mechanical pulps. Pigment colorants, usually formed by precipitation or ‘laking’ of organic dye molecules, require the use of a retention aid, as in the case of the mineral fillers. Papermakers favor pigment colorants for products that have to resist fading on exposure to light.

Fluorescent whitening agents, often called ‘optical brighteners,’ are chemically very similar to certain direct dyes. However, they have the special ability to absorb light energy in the ultraviolet range and reemit some of that energy in the visible, blue part of the spectrum.

Process Additives for Papermaking

Retention and Drainage Additives

Papermaking involves separation between a solids-rich phase, the paper web, and a liquid-rich phase, the white water (*see Papermaking: Overview*). Chemicals that make this separation occur more completely or more quickly are called ‘retention aids’ and ‘drainage aids.’ There is so much overlap between the chemicals that perform these two functions that it makes sense to discuss them together. In colloidal chemical terms most of these additives can be grouped within the categories of coagulants, flocculants, and colloidal particles.

Coagulants

During papermaking one function of a chemical coagulant is to neutralize the surface charge of suspended materials and remove electrostatic barriers, preventing them from colliding with each other and sticking together. Because the fibers and many other materials used for papermaking typically have weak negative charges at their surfaces, coagulants usually consist of multivalent cationic materials, which can be either soluble inorganic products or organic polymers.

Among inorganic coagulants, the most widely used is aluminum sulfate, or 'papermakers' alum.' Alum derives its coagulating ability from the trivalent character of aluminum, plus a tendency to form oligomeric species. The system pH, contact times, and temperature profoundly affect alum's performance, with best results often obtained in the so-called 'acidic' range of papermaking, between pH values of 4 and 6. Polyaluminum chloride (PAC) and related products have extended the range of efficient coagulation to somewhat higher pH values.

The most important polymeric coagulants are the polyamines, including polydimethylamine-epichlorohydrin, as well as polyethylenimine (PEI) products and poly-diallyldimethylammonium chloride (DADMAC). The common feature of these polymeric coagulants is their high positive charge density, often with 100% of the monomeric groups bearing a charge. Molecular masses typically range from hundreds of thousands to about two million grams per mole.

Flocculants

The function of a flocculant is to cause suspended particles to stick together very strongly after coming into contact. The effect is achieved by use of very-high-mass polymers, which are capable of forming molecular bridges between the adjacent surfaces. When papermakers use the term 'retention aids,' they most often mean linear copolymers of acrylamide. Molecular masses of these retention aids range from about 4 million to upwards of 20 million g mol^{-1} . Retention aids with a wide range of charge density, either positive or negative, are widely used. Retention aids are most commonly delivered to the paper mill in the form of a water-in-oil emulsion, which needs to be inverted at high levels of dilution and agitation before it can be used. It is common to add a retention aid flocculant near the end of the wet-end process, after furnish has been conditioned by the addition of a lower-mass coagulant.

Colloidal Particulates

Since the 1980s there has been a trend toward the use of colloidal 'microparticles' or 'nanoparticles,' including colloidal silica and montmorillonite clay products. Under the right conditions, these have the ability to interact with the flocculants just discussed, producing a pronounced increase in drainage rates during paper formation.

Deposit Control

Papermaking operations are vulnerable to problems resulting from the deposition of tacky and pitch-like materials on to the equipment. In addition to talc, as already mentioned, deposit-control additives include organic detackifying agents, dispersing agents, and barrier chemicals. Effective use of a retention aid program, as just discussed, also helps to avoid deposition of fine materials on to chests, pipe walls, headbox surfaces, and in press felts and related equipment. Organic detackifiers include soluble polymers, such as polyvinyl alcohol products, designed to adsorb on to oil-loving surfaces and make them less tacky. Dispersing agents, including nonionic surfactants composed of short ethylene oxide chains attached to oil-loving groups, can be used to overcome deposition of tacky materials at specific locations in a papermaking process. The term 'barrier chemicals' describes materials sprayed directly on to the surface of a forming fabric or press felt to overcome deposit problems. Highly cationic polymers, i.e., organic coagulants, are used alone or in combination with surfactants to achieve this effect.

Biological Control

Papermaking systems, with their warm temperatures and content of starch and other biodegradable materials, can provide a wonderful medium for the growth of bacterial and fungal slime. Slime can become entrained and cause holes and breaks in the paper web, in addition to spots and bad smells. The two main categories of chemicals that papermakers use for slime control are oxidants and toxic organic chemicals. Chlorine dioxide has become a favored oxidant, especially for paper grades that use bleached kraft pulp. The selection of slimicides depends on factors such as temperature, the kind of slime in the system, and issues of effectiveness and biodegradability of the added material.

Foam Control

Due to the presence of air, water, high degrees of agitation, and various substances that can stabilize bubbles, there is the potential for severe foam problems during papermaking. Some of the problems

can be minimized by avoiding overuse of surface-active materials and water-soluble polymers such as starches and wet-strength agents. Chemical defoamer formulations typically contain water-insoluble surfactants. They can also contain hydrophobic particles that help to rupture bubble surfaces when the surfactant molecules spread across those surfaces.

See also: **Packaging, Recycling and Printing:** Paper Recycling Science and Technology. **Papermaking:** Coating; Overview. **Pulping:** Chemical Pulping; Fiber Resources; Mechanical Pulping; Physical Properties.

Further Reading

- Eklund D and Lindström T (1991) *Paper Chemistry: Introduction*. Grankulla, Finland: DT Paper Science.
- Lindström T (1989) Some fundamental chemical aspects of paper forming. In: Baker CF and Punton VW (eds) *Fundamentals of Papermaking*, pp. 311–412. London: Mechanical Engineering Publishing.
- Neimo L (1999) Papermaking Chemistry. *Papermaking Science and Technology*, vol. 4. Helsinki/Fapet Oy, TAPPI Press.
- Roberts JC (ed.) (1996) *Paper Chemistry*, 2nd edn. London: Blackie.
- Scott WE (1996) *Principles of Wet End Chemistry*. Atlanta, GA: TAPPI Press.
- Smook GA (1992) *Handbook for Pulp and Paper Technologists*, 2nd edn. Vancouver, Canada: Angus Wilde.

Environmental Control

D Peterson, Western Michigan University,
Kalamazoo, MI, USA

© 2004, Elsevier Ltd. All Rights Reserved.

Introduction

The basic operations of the paper industry involve the conversion of renewable resources using chemicals, energy, water, and human ingenuity to produce a universal consumer product. Wastewater, air emissions, and both dry and waterborne solids are generated during the process. Heat and noise also are generated and disbursed into the environment. The objectives of this article are to identify the sources of these emissions and the processes by which they can be managed.

An overview of the paper manufacturing process suggests that the sequence of events can be divided into distinct phases. The first phase involves the

recovery of papermaking fiber from either wood or recycled fiber resources. The second phase involves the purification of the liberated fiber and preparation of that fiber for the papermaking process. The final phase includes formation of the paper mat and modification of its surface to meet specific moisture resistance, strength, and optical properties for designated paper or paperboard applications.

The pulping operation and papermaking operations often run at separate locations, while integrated operations combine both pulping and papermaking facilities at one manufacturing site. The pulping phase is accomplished using several different processes ranging from full chemical pulping to thermal and mechanical defibering with a large variety of sequential treatment combinations involving chemical, thermal and/or mechanical processes in between. The chemical pulping operations often are accompanied by a variety of complex chemical recovery processes depending on the chemicals involved.

The fiber purification processes involve both mechanical and chemical processes to remove unacceptable components and to brighten the fiber for specific applications.

The papermaking phase commonly involves the dispersion of the fiber in large quantities of water and other additives to modify optical, chemical, and physical properties. The thin slurry is distributed on a continuous moving forming fabric allowing the water to separate from the wet fiber mat. The wet mat is then pressed against an absorbent fabric to dewater the wet mat. The partially dewatered mat is dried by evaporating most of the remaining moisture to form a paper or paperboard sheet.

Depending on the use of the paper it may also have been surface treated with sizing to minimize moisture penetration and to prevent ink from feathering on a printed page or coated with additional material and/or treated mechanically to modify its surface and optical properties. Coating followed by calendaring are common treatments to obtain papers with excellent printing quality characteristics.

Before dealing with the treatment of some specific waste streams, it is important to recognize some of the waste streams that are characteristic of the production phases. Characterizing each of these by-product streams and assessing their reuse alternatives will enable the diversion of some of the waste streams to reuse elsewhere in the manufacturing sequence.

The following figures (**Figures 1 to 5**) depict several of the steps in the production of paper and identify some of the major emissions from the various stages. The process schemes describe the liberation of fiber from wood or the recovery of fiber from recycled paper sources (post consumer) through