Use of fillers in papermaking

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There is a wide choice of fillers available to reduce the material costs for such commodity fine papers as offset, xerographic copy, etc. Many are compatible with an acid or an alkaline system.

It is probable that the first filled sheet of paper was made by Ts'ai Lun, although it was not done purposely. He just did not have the equipment for proper cleaning, and thus his paper was a "victim" of the system. Since Lun's efforts were well before the time of Johann Gutenberg, Chester Carlson, and George Eastman, he had little to worry about the contributions of fillers to the qualities of, respectively, printing papers, xerographic copy papers, and photographic base papers. Compared with the present day papermaker, he also had little to worry about in the selection of the filler, whether to use an acid or alkaline papermaking system, what type of sizing agent or retention (drainage) agent to use, what problems he might encounter with contamination or abrasion or recovery, and whether the use of a filler truly had all of the economic advantages he thought.

It is not the purpose of this article to trace the history of the use of fillers in paper. Its focus, rather, is on the state of the art, primarily in the use of relatively low levels of filler (up to 30%), with a brief description of efforts toward the use of filler at levels of 50+% up to 100%. Volumes have been written about the many considerations in the manufacture of filled papers. This article draws on many published works and limits the reporting primarily to the materials rather than to the process and its associated variances. Wherever possible, reference is made to production rather than to laboratory practice.

Why use fillers?

The primary reason for the use of fillers is economics. For many or most uses, fillers are less expensive than cellulose fibers. Johnson (*1*) reports that this is particularly true in Europe, where a combination of alkaline sizing, the ready availability of chalk or ground limestone, and the high cost of imported fiber has promoted the conversion of 40–50% of commodity fine paper grades to filled sheets. Most European mills can cut costs by substituting calcium carbonate for clay at equal filler loadings. Clay is less expensive than calcium carbonate in North America, so most North American mills must be able to increase filler loadings to justify a conversion to alkaline sizing—and calcium carbonate—in these same paper grades.

Abell (*2*), who challenges the switch to alkaline sizing and calcium carbonate as being more costly than just the material savings, cites a new list of problems that face the papermaker during a conversion to alkaline sizing. He suggests that the old standby rosin size can be successfully used in a neutral sizing system, but with other pigments. The pros and cons of the various sizing methods are discussed later in this article.

Busker (*3*) states that, in North America, the relative pricing of paper versus fillers favors a long-term trend toward increased use of filler and that some papers, such as printing grades, may depend on fillers to achieve opacity and brightness and to offer desirable printing qualities.

Economics is not always the determining factor. An example would be photographic paper base, where the incorporation of a filler such as titanium dioxide is instrumental in preventing show-through of the photographic image on the reverse side of the print. Until fairly recently, titanium dioxide was the only filler of sufficient optical density and sufficient "whiteness" and color stability to be used in photo base. Alkaline sizing does permit a broader selection of fillers, particularly those of recent modifications for high brightness and stability. Similarly, high-grade offset papers require qualities where economics is not the determinant.

Selection of fillers

Filler selection is based primarily on the end result desired. Selection is also based on the current sizing system being used in the mill and the desirability of changing that system, if necessary, from acid to alkaline (with the associated changeover problems). Obviously the use of calcium carbonate is prohibitive in an acid system. (The author proved this to his dismay—and to the enjoyment of others—when he momentarily forgot his high school chemistry and dumped several gallons of aluminum chloride into a machine chest filled with pulp and calcium carbonate.) Most of the pigments such as titanium dioxide, clay, talc, and the silicates will tolerate an acid system. However, for a given level of the same filler, an alkaline sheet has an inherent strength advantage over an acid sheet.

House (*4*) classifies the various natural and synthetic minerals that can be used in paper into three categories:

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- Titanium dioxide: used to increase the brightness and opacity of paper
- Titanium dioxide extenders: used to reduce or eliminate the use of titanium dioxide. These materials, which are less expensive than titanium dioxide, also increase the brightness and opacity of paper. Such materials include calcined clay, precipitated calcium carbonate, alumina hydrate, and amorphous silica.
- Primary fillers: used to minimize cost without adversely affecting quality by minimizing the use of titanium dioxide, fibers, or expensive additives and to improve machine runnability.

House suggests asking the following questions when selecting a filler:

- What are the sheet specifications required by the customer?
- What are the filler options?
- Which filler will meet the sheet specifications?
- Which filler is the most cost effective in meeting the sheet specifications?

He found that filler clay, standard delaminated clay, coarse delaminated clay, talc, and two fine-ground limestones were acceptable for 15-lb bond. Coarser pigments are more cost-effective primary fillers than the finer pigments and generally give higher strengths, thus permitting the papermaker to replace more fiber.

Further criteria for filler selection are presented later in this article, including filler pretreatment for high-load-content papers.

Other fillers

The primary purpose of this article is to discuss the use of fillers (and the processes for their use) in commodity fine paper grades, such as copy bond and offset. These fillers usually are inorganic minerals. However, it seems that almost every insoluble organic polymer that can be prepared in powdered form has been evaluated as a filler—usually for special properties—in paper, at least in handsheets. Probably the best known, at least in reaching commercial paper manufacture, were the Dow Microspheres, which encapsulate minute amounts of gas inside a styrene copolymer sphere. Upon exposure to heat in the drying section, the gas expanded, inflating the spheres. The result was a low-density sheet that was of interest as a copy paper when postage rates were a matter of concern. Unfortunately, it was difficult to obtain an adequately smooth surface and their use was discontinued.

As an example of a novel filled paper, Kurata and Kubojima (*5*) have prepared a ceramic paper with high filler content that sinters at temperatures below 900°C. In producing the paper, simultaneous additions of polyanionic and polycationic agents increased filler retention. The addition of a water-insoluble flux lowered the sintering temperature.

Of course carbon black fits into the filler category, although not for the purposes of this article. Quite high levels of carbon black are used to obtain high opacity and/or good electrical properties. It has been shown that addition of minute amounts of carbon black to certain furnishes incorporating brightener can improve the "apparent whiteness" of the sheet.

Cationic starch

The uses of cationic starch for retention, dispersion, strength maintenance, etc., are described throughout this article. To avoid redundancy, we state here only that the use of this material is critical to the process of manufacturing filled papers, particularly as the level of filler added is increased.

Role of fibers

It is not probable that a papermaker will, or even can, make a major change in the fiber content of a sheet to accommodate filler. The primary qualities of the sheet are, after all, dependent upon the fiber, its preparation, and its formation into a sheet. Fillers are usually added to reduce fiber content. This does not mean that some consideration should not be given to selecting the best pulp type.

Pulps of higher chemical purity are more difficult to size than higher yield pulps. Similarly, kraft pulps are more easily sized than sulfite pulps. The primary difference is associated with the ion-exchange and the sorption capacities of the cellulose. This appears to be regulated by the carboxyl and other reactive groups associated with the hemicellulose fraction (*6*). Hemicellulosics can be removed by any of the conversion processes that take place during pulping and bleaching, and this increases the resistance in sizing the pulp. Conversely, some chemical pulps may be more readily sized if they do not contain some of the more coordinated organic anions, such as lignosulfonic acid and oxalic acid (*7*).

Thus, the ideal pulp for a filled sheet would be a long, unbleached, well-hydrated, softwood kraft fiber. Alternatively, one would select from a series starting with the bleached softwood kraft pulps and ending with the high-alpha-cellulose bleached hardwood sulfite pulps.

Selection of sizing system

The need to size a sheet against penetration of liquids is well known, and the processes for sizing are quite well understood and described in the literature. Griggs and Crouse (*8*) have described the various types of sizing, from the normal acid type (rosin, wax, fatty acid), which is a nonreactive or bulk type, to the newer cellulose-reactive alkaline sizes (alkyl ketene dimer, alkenyl succinic anhydride). They also described the factors influencing sizing response, such as hydrophobic-reactive functional group interactions, hydrodynamic shear, system closure, drying, etc.

Morris Illig invented rosin sizing in 1804, and many mills still use it today, usually in an acid system with alum. Most fillers can be used with an acid system, with the exception of calcium carbonate. However, the use of fillers in such a system invariably results in a loss of strength, particularly burst. House (*4*) suggests that it is possible to use rosin in a neutral/alkaline system and not go through the "horrors" of converting to a cellulose-reactive size. Such a system can tolerate the moderate amounts of carbonate typically found in recovered coated broke. Two problems occur in a neutral/alkaline system: (a) a loss of size retention as the pH approaches 4.5+ and (b) an adverse effect of soluble calcium on rosin size. To prevent loss of the size, House recommends the use of a cationic retention aid. To minimize the effect of the calcium ion, he recommends maintaining the stock prep system at pH 6.0+. When calcium carbonate is added as a filler, it should be added as close to the headbox as possible and after the alum and size.

Alum, which is normally the acidifying agent, can be used to advantage in a neutral or alkaline system. Strazdins (*9*) reports that the use of moderate amounts of alum produce several beneficial effects, including increased sizing, better drainage, higher retention, and better runnability. Admittedly, there is still considerable mystery about how the various types of alumina that are formed improved the performance qualities of alkaline sizes, cationic starches, and retention aids. Alum can be added at the wet end to the thick stock (usual), the thin stock, or the recycled tray water to promote better retention and to promote stabilization of the alkenyl succinic anhydride (ASA) size particles. Beneficial effects have been obtained by adding alum to cationic starch after the starch has been solubilized, or by adding alum to an already prepared cationic ASA emulsion. Strazdins also presents data showing that the slightly negative charge mobility (-0.3) produced by adding small amounts of alum (e.g., 0.5%) to an ASA/cationic starch can result in a significant (40%) improvement in sizing of a carbonate-filled sheet.

The shift to alkaline sizing is particularly evident in Europe, where carbonate fillers are readily available. The advantages of alkaline sizing include the ability to increase the filler content without sacrificing strength, reduced energy usage, improved runnability, and improved paper quality, including heat and light stability. The two most popular alkaline-sizing materials are the alkyl ketene dimers (AKD) and ASA. Both of these are cellulose-reactive sizes.

The AKD has a general formula:

$$(RCH = C = O)^2$$

where R is a long-chain aliphatic group. At pH 6.5–6.8, this group reacts with the cellulose hydroxyl group to form a stable ester linkage. AKDs are water insoluble and are therefore used in emulsion form. A cationic starch is commonly used to make an emulsion of AKD when it is used internally. This both emulsifies the size and imparts a new positive charge to the particles formed. The electrostatic potential that develops between the positive particles and the negative fibers creates an attraction between the two. This reaction occurs during the drying operation on the paper machine.

ASA is also a water-insoluble liquid that must be added as an aqueous emulsion. A cationic starch is often used as the dispersion medium. Like AKD, ASA is a chemically reactive size with the cellulose hydroxyl groups. Wasser (*10*) explored the variables that affect the hydrolysis and cure rate of this material and found that while the ASA emulsions were most stable at low temperature (25°C) and low pH (3.5–4.0), the cure rate was best at temperatures above 60°C and at a pH above 7.

Farley (*11*) has summarized the behavior of AKD and ASA in several important areas.

Emulsion stability. AKD is stable enough to be shipped by the manufacturer. ASA must be made in the mill.

Mixing with stock. Both AKD and ASA must be thoroughly mixed with the stock to minimize size usage and improve runnability.

Attachment to fiber. Both AKD and ASA require a low-molecular-weight cationic polymer and/or cationic starch in the preparation of emulsion.

Retention. First-pass retention is critical. If the size is not retained, the recirculating size is subject to hydrolysis and emulsion breakdown, resulting in poor sizing, runnability, and sheet quality.

Cure. ASA almost always cures much faster than AKD, providing better sizing prior to the size press. Both cure to essentially the same level off the machine although, under given conditions, the ASA approaches final level more rapidly.

Dumas (*12*) warns of the differences that will be encountered when switching from acid sizing to alkaline sizing. Some of the differences are beneficial, some are detrimental, and some are just different. It is important to be prepared for—but not scared of—these changes to maximize productivity and profits. The author has found that this can be done by taking advantage of the wealth of experience in the industry. Almost any good papermaker is willing to share with you.

Retention aids

Retention aids not only serve the purpose of retaining fillers in the sheet. They also are important to retention of the sizing agent. Moodie (*13*), in his review of the literature, found that retention aids have been proposed to function through a number of mechanisms:

- Filtration/mechanical entrapment
- Coagulation (or charge neutralization)
- Flocculation

The first mechanism is primarily a physically controlled process and is related to wire mesh, basis weight, and the hydrodynamic forces at the point of sheet formation and on the table. Coagulation is the primary step for chemically-induced retention. Alum and sodium aluminate are the primary inorganic coagulants in an acid system. However, the aluminum is ineffective for charge neutralization in an acid system, and it is necessary to use a synthetic organic coagulant. These are highly cationic, low-molecular-weight (50,000–200,000 mol. wt.) substances (usually polyamines) designed to operate over a broad pH range.

The most common retention aids today are the high-molecular-weight acrylamide-based polymers with molecular weights of 500,000 to tens of millions. Unlike coagulants, which are always cationic, these flocculants can be anionic, cationic, or nonionic. A variety of each of these materials is available to accommodate the unique needs of any paper machine. Moodie and Drew (*14*) insist that, after consultation with a supplier, the evaluation process *must* move into a laboratory equipped with a dynamic drainage jar. One can then evaluate the proper amounts and the best order of addition for each of the components so that the proper ionic balance can be obtained for optimum retention of fiber, filler, and size commensurate with good drainage. When the lab work is complete, and only then, take your proposed system to the paper machine. Paper machines, being frequently of their own mind, will require some further balancing for best performance and product quality, but the "cats will have been separated from the dogs" back in the lab.

High-filler-content papers

Up to this point, the focus has been on the manufacture of papers containing up to 25–30% filler. However, there has been considerable effort aimed at levels of 50–80% filler without destroying basic sheet properties. Some work has been carried out with "lumen loading" for a 100% filled sheet. Most of these processes require abnormally high levels of a cationic starch, a water-soluble cationic polymer, and/or latex to the furnish.

Lindstrom and Kolseth (*15*) provide a simple recipe for making a sheet with 30–80% filler while maintaining good breaking strength and rattle:

- Open the filler addition valve.
- Open the wet-end starch valve.
- Open the valve for the retention aid.

They do suggest that opening all three valves at once may be a little daring, but opening them a little bit at a time in the given sequence is proper. The starch of choice is of the cationic variety, with an anionic polyacrylamide used as the retention aid. The basic problem is to select a system that (a) is compatible with other additives and (b) allows a high level of starch addition. (The final sheet may contain 15% pulp, 80% filler, and 5% starch.)

Mather and Jones (*16*) report that pretreatment of a clay filler with a suitable cationic starch can permit a substantial increases in filler loading without loss in strength and with better control of the tendency for dusting. Cationic starch is used instead of synthetic flocculants because the dose rate does not have to be controlled as carefully. This process, known as the Hylode system, is used extensively in Europe.

Either cold-water-soluble or cooked cationic starch may be used. A 5% starch solution is mixed with a 35% clay/water dispersion in a high-shear in-line mixer to obtain a final ratio of 5% dry starch on 5% clay. The treated clay dispersion is preferably added at the fan pump box.

Post (*17*) has patented a process for manufacturing fine paper using an acidic paper furnish, 30–70% mineral filler, at least one water-soluble polymeric retention aid, and 3–7% (based on dry furnish weight) of a cationic latex or an amphoteric latex that is cationic at acid pH. The filler can be kaolin clay, talc, titanium dioxide, aluminum hydrate, hydrated silica, and mixtures thereof. The latex can be a styrene butadiene, acrylic, or polyvinyl acetate, with the restriction that it provide good mineral retention, that it have a charge opposite to and less than the sum of charges of the other ingredients in the furnish, and that it precipitate on the fibers and fillers to exhaustion. Excellent sheet quality, including strength, printability, and coatability, is claimed.

Finally, Miller and Paliwal (*18*) have described lumen loading as an approach to 100% filler retention. Their process involves vigorous agitation of a pulp in a concentrated suspension of filler and then washing the pulp to remove all filler external to the lumen. The addition of a retention aid such as polyethyleneimine (PEI) is helpful in retaining the filler in the lumen in the washing stage. The most significant difference between paper made with lumen loading and conventionally filled papers is the higher tensile strength, stiffness, and tear of the lumen-loaded paper. Lumen-loaded paper showed a slightly lower brightness and opacity, particularly with an increase in filler content. This handsheet work was done with southern pine kraft (dried and never dried; bleached and unbleached; beaten and unbeaten) loaded with titanium dioxide and clay (separately). Up to 25% loading was obtained with titanium dioxide and PEI, and scanning electron micrographs show the filler to be located in the lumen and pits of the fiber, with the external surface essentially free of pigment.

Summary

There is a wide choice of fillers available to reduce the material costs for such commodity fine papers as offset, xerographic copy, etc. Most of these fillers are compatible with an acid or an alkaline system, although the use of calcium carbonate in an acid system must be minimized. The addition of fillers reduces the strength and, at high levels, the feel of the paper. However, available technology permits the use of 50% or more filler without substantial loss of strength or feel.

The strength loss is not as great in an alkaline system as in an acid system. In either system, the addition of cationic starch reduces the strength loss. The preferred system involves the use of a cationic starch with (a) a cationic, cellulose-reactive sizing agent and (b) an anionic retention aid, with charge reversal occurring just prior to forming.

North America seems to be following the lead of Europe in converting to alkaline-sized filled sheets. A substantial number of paper mills will probably be converted by the year 2000. The conversion from an acid to an alkaline system is not simple, but once it is made, the ability to use higher filler content without sacrificing strength will provide economic advantages that outweigh the headaches of conversion.

The paper industry—at a technical level—is communicative. The suppliers are helpful on site in the mills, and papermakers have a format for sharing their experiences at TAPPI conferences and seminars. Attendance is recommended.

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