CHAPTER 1

Microparticle Programs for Drainage and Retention

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INTRODUCTION

When papermaking technologists use the word “microparticles,” usually they mean certain chemical additive programs that can promote the release of water and help retain fine particles during formation of paper. The prefix “micro” is actually somewhat of a misnomer; some of the most commonly used particles, for which this technology is named, have primary diameters in the nanometer range, 1-5 nm [1-4]. Microparticles, as well as certain analogous papermaking additives that we will call “micropolymers,” are effective only when used in sequence with certain oppositely charged high-mass polymers, hence the term “microparticle programs” as used above.

This present book serves as a witness to explosive growth. Before 1980 the subject of microparticle technology, as we know it today [5-6], did not exist. Papermakers were generally unaware of potential uses of such additives as colloidal silica and bentonite, except for their occasional uses in water treatment [7-8] or for control of paper’s frictional properties [9]. Now there are at least 550 paper machines that have used these two types of very finely divided minerals – in sequence with cationic starch or cationic acrylamide copolymers - to promote drainage and retention [10]. About 300 have been reported to use colloidal silica [11], and about 250 have been reported to use bentonite [10]. In addition, there are various paper machines that have used, or are currently using, related retention and drainage programs with highly cross-linked anionic polymers [12] or lignin byproducts playing the role of microparticle [13].

The purpose of this introductory chapter is to review the already-extensive literature related to microparticle programs. This includes descriptions of the materials, how they work together mechanistically, and how the papermaker can take advantage of them to increase paper production rates or product quality.

Defining Characteristics of Microparticle Additive Programs

The most striking and common observation associated with introduction of microparticle programs to paper machine systems is a pronounced increase in the rate of dewatering [3,6,13-31]. Unsuspecting paper machine operators sometimes have been surprised by rapid and large shifts of the dry-line on a Fourdrinier paper machine when the flow of a microparticle additive begins. Though there exist more conventional chemical approaches to improving drainage on paper machines [32-34], the effects produced by microparticle programs have a tendency to be more abrupt or dramatic. Accordingly, papermakers have coined terms such as the “microparticle effect” to describe what happens when the right furnish conditions have been established and then microparticles are added [14,19,25].
But what are those “right conditions” that must be in place so that the characteristic drainage improvements and other commonly observed benefits can follow? As you will see in the pages ahead, there is beginning to be more and more variety in the available microparticle programs. However, it still is possible to set out some common attributes, as follows [11,16,24-26,35]:

1. A high-mass polyelectrolyte, usually of positive charge, is added, most often to the thin-stock furnish of a paper machine system. The polymer must have a high affinity for the fiber surfaces, as well as a tendency for loops and tails of polymer to remain extended out into solution for at least several seconds after it has become adsorbed [6,36-38].

2. The furnish encounters one or more unit operations having a high level of hydrodynamic shear after introduction of the high-mass polyelectrolyte to strongly disperse polymer-induced fiber flocs [2,6,11,21,26,39-45]. For example, the stock may flow through a pressure screen, or perhaps there is sufficiently high shear in a hydraulic headbox [46].

3. Small, solid or highly branched, highly charged and usually anionic particles or polymers are added to the system. It is most common that the microparticle is added after steps “1” and “2,” but, as we will see later, other options are known [7,18,22,47-54]. The word “microparticle” will be used here in a broad sense to include both solid materials and polymers that act similarly to the solid particles. To be effective, microparticles should have a high specific surface area, e.g. 500-1200 m²/g in the case of certain colloidal silica products [3]. In the case of solid particles, this high surface area implies that at least one dimension of the microparticle should be less than about 5 nm [19,55-56].

For purposes of the present discussion, items 1-3 will be considered primary defining characteristics of microparticle programs. Some secondary attributes of microparticles systems may include the following:

4. There is a tendency for the most promising results to be achieved at a certain ratio of high-mass polymer to microparticle, though this ratio may shift as a result of changes in the electrokinetic charge balance of the furnish [11,19].

5. Closely related to the previous item, many microparticle systems also have been found to have optimum effectiveness at or near the point of charge neutralization in a papermaking furnish [57-58].

To complete the list, several effects are commonly observed upon implementation of a microparticle program:

6. An abrupt increase in the rate of water release from the paper web during forming and pressing when the microparticle additive flow is started (or vice-versa).

7. Observations that fiber flocs tend to form in response to the addition of microparticles, even in cases where an original set of polymer-induced fiber flocs have been redispersed [36-37]. However, the flocs formed upon introduction of the microparticles are (a) less harmful to formation uniformity, (b) often more easily redispersed by moderate flow, as in the headbox, and (c) more capable of forming again after being dispersed by shear [16,52,59-62].

8. Reported instances of formation uniformity improvement, often associated with either (a) reduced headbox solids, (b) increased refining, or (c) a shift towards use of
fiber with a shorter fiber length, following introduction of the microparticle program [16].

9. A tendency for the paper to be more porous after implementation of a microparticle program [16,21], though such effects may be partly obscured by size press and calendering operations.

The list above raises fascinating questions. Why, for instance, does hydrodynamic shear seem to play such an important role? And what is the explanation for the reversibility of microparticle-induced flocs? Those questions will be considered after we consider the main types of materials used in microparticle programs. However, let us first review the main benefits that researchers and papermakers have observed following implementation of microparticle programs.

Motivations for Implementation of Microparticle Programs

“Improved drainage and retention without wrecking formation uniformity” – this is what papermakers and their customers want. But, you may ask, does microparticle technology make sense for a particular paper machine and paper grade in which you may be involved? To answer that question one needs also to consider some cost and risk issues.

Reasons for caution: Let’s first consider the issue of net chemical costs. It has been argued that dual-polymer systems, including microparticle systems, usually require up to twice as much net chemical, compared to single-component, synthetic retention aids [63]. The higher net dosage may be due to some kind of “competition” between the respective additives. Indeed, some very effective strategies for the use of microparticles involve reversing the surface charge of materials in the furnish from net negative to positive [22,64]. Thereafter, additives such as colloidal silica or bentonite will tend to reverse the charge to net negative once again. In principle, it takes more charged chemical to reverse the zeta potential twice, compared to conventional drainage chemical approaches the involve neutralization of charge [16,33-34].

The next issue is complexity. Any time that a paper mill goes from a single-additive system to a two-additive system there are twice as many feed pumps, valves, flowmeters, and pipes to deal with. Rather than controlling just one addition rate of retention aid, now an operator must be aware of two different flows, as well as the ratio between them. A later section of this chapter will touch on strategies to optimize microparticle programs, but for now let’s consider increased complexity as something that discourages their implementation in some cases.

The final issue that leads some papermakers to favor drainage chemical programs without microparticles relates to issues of process stability. Consider for a moment some of the “defining characteristics” listed in the previous section. These included charge-sensitivity and a tendency to accelerate drainage rates markedly, especially when the system is in balance. These characteristics suggest instability, especially if there are no automatic controls of addition rates. Solutions to this kind of issue will be considered in the final section of this chapter.

Reasons to go ahead: Publications state various motivating reasons to implement microparticle-type additive programs in paper mills. Table 1 lists such assertions roughly in order of how often they have been mentioned in the literature. Though this sampling of the literature is incomplete, it gives insight into the priorities of
various authors. As shown, the most widely claimed benefits of microparticle programs were increased retention (48 times mentioned), increased drainage (40 times), improved formation (21 times), dry strength improvements (9 times), and increased solids after wet-pressing (8 times).

<table>
<thead>
<tr>
<th>Type of Claimed Benefit</th>
<th>Literature References</th>
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<tr>
<td>1. Improved retention, <em>i.e.</em> the use of microparticle programs to improve retention of fine particles</td>
<td>2-3,5-6,11,13,16,21,23,28,30-31,38-41,43,47,54,58-59,62,65-90</td>
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<tr>
<td>2. Speed increase on drainage-limited paper machines due to faster dewatering in the forming section</td>
<td>3,6,13-16,18-19,21-22,24-25,28-29,31,39,41,43,57-59,66,68,73-74,76-78,80-81,83-84,86,91-97</td>
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<tr>
<td>3. Improved formation uniformity due to such factors as reduced headbox solids and a different flocculation mechanism</td>
<td>5,11,13,15-6,23-24,29-30,40,59,69,72,74,79,81,90,96,98-100</td>
</tr>
<tr>
<td>4. Increased dry strength due to such factors as allowing cationic starch to be retained more effectively or at higher levels</td>
<td>5,20,30,66,75,83,101-103</td>
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<tr>
<td>5. Speed increase and/or reduced drying energy due to improved dewatering in the wet-press section</td>
<td>16,21,25-26,28,39,75,92</td>
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<td>6. Reduced paper machine downtime due to less deposits of tack materials or less frequent web breaks</td>
<td>21,41,67</td>
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<td>7. Pollution abatement and reduction in the amount of biological oxygen demand (BOD) in mill effluent</td>
<td>79,104,105</td>
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<td>8. Reduced variability of paper machine operations and resulting paper physical properties</td>
<td>24</td>
</tr>
<tr>
<td>9. Improved saveall performance, possibly related to ability of the flocs to re-form after breakage</td>
<td>67</td>
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**TYPES OF MICROPARTICLES**

Figure 1 illustrates typical sizes and shapes of the most common microparticles in current use. Pictures can help one to appreciate the very small dimensions involved with colloidal silica, bentonite, and other related materials. For a more detailed perspective, Moberg [106] published a series of increasingly enlarged views of a hypothetical fine papermaking furnish. Each enlargement decreased the scale by a factor of ten. A key point of the exercise was to drive home the point of how incredibly small these particles are – even when compared to filler particles.
Chemistry related to the manufacture and use of colloidal silica is described in a book by Iler [55]. Briefly stated, colloidal silica is prepared by partial acidification of monomeric alkali silicate solutions. Limited acidification, with the pH kept above the neutral point, is expected to yield individually dispersed particles of silicon dioxide, also known as “silica sols.” “Aging” the mixture can increase particle size. Acidification to lower pH values is generally expected to yield more mutual agglomeration, leading to chains or clusters of the primary particles; these are also known as “silica gels.” Due to the presence of acidic silanol groups, colloidal silica particles have a negative surface charge, which increases with increasing pH [55].

**Early uses of colloidal silica in paper:** Years before its application for drainage promotion in paper, an essentially similar technology already had been disclosed as a binder for wet-laid nonwoven products formed from non-cellulosic fibers. A 1966 patent by Bodendorf and Osborne [107] described a binder system based on addition of cationic starch, followed by colloidal silica to a slurry of inorganic fibers. Unlike cellulosic fibers, the inorganic fibers do not bond together effectively in the absence of some kind of binder.

In 1969 Colom Pastor and Martinez Martinez [9] published an intriguing finding that addition of colloidal silica to a papermaking furnish increased the retention of talc filler. The main goal of the project was to control frictional properties and other physical attributes of the paper. Though it might seem that these researchers had stumbled onto an early form of microparticle program, as defined earlier in this chapter, their work did not involve any kind of organic polymer. Rather, it appears that the reported retention
benefits of the colloidal silica addition may have been related to a charge optimization in a system that had been overdosed with alum.

Another relatively early mention of silica addition to a paper machine system to retain something involved treatment of white water [48]. Combinations of a highly cationic polymer, anionic particles such as activated silica or bentonite, and finally a high-mass anionic polymer were used to clarify the white water to allow its reuse in such applications as showers.

A “microparticle program” for papermaking emerges: The first true microparticle program, according to the criteria given earlier, was disclosed in the early 1980’s [83]. Sunden et al. [101] patented the use of cationic starch and colloidal silicic acid (i.e. “colloidal silica”) in certain ratios as a binder for paper. The colloidal silica particles were specified as being smaller than 20 nm and the cationic starch was specified as having more than 1% of cationic charge. A typical value for mean particle size of this kind of silica sol is 5 nm [2-3,14,83]. In Iler’s terms [55] one would describe those particles as “sols,” i.e. individually dispersed singlets.

Regarding the order of addition of these chemicals, one of the earliest patents offers a surprise. Svending et al. [50] specify adding the colloidal silica first, followed by cationic starch, and then the rest of the silica. As we will see, most present-day applications are limited to single-point addition of microparticles, not split-addition.

Anionic aluminum- and boron-containing or treated silicas: Users of the earliest colloidal silica microparticle products found that drainage and retention benefits decreased with decreasing pH [83]. The effect of pH apparently is related to the amphoteric nature of silica and other oxides; the zeta potential tends to be high and negative under neutral and alkaline conditions, but it loses much of its anionic surface charge when the pH is reduced to 4-5.5, a typical range for acidic papermaking. In principle the problem can be overcome by coating the particles with something yet more anionic. One such substance is aluminum silicate [108-111], or in more general terms “aluminum-modified silicic acid.” This composition can be prepared, for instance, by adding sodium aluminate to sodium silicate solution [14]. Best results were found with particles having a specific surface area in the range 300 to 700 m²/g. Such microparticles are reported to work well with cationic acrylamide copolymers under acidic as well as alkaline papermaking conditions [14,59]. The improved performance has been attributed to an increased anionic character of the colloidal silica resulting from isomorphous substitution of charged Al(OH)₄⁻ groups in place of structurally identical neutral Si(OH)₄ groups.

A recent report describes use of colloidal borosilicate inorganic oxide sols to promote drainage, retention, and paper quality [112-113]. Boron is similar to aluminum in having three valence electrons. Further comparative study is needed to determine the relative advantages of colloidal silica products with differing amounts of either boron or aluminum over a range of pH values.

Drummond patented an alternative approach in which anionic sols were prepared by combining aluminum sulfate, aluminum chloride, or similar materials to alkaline silicate solutions and related materials [114]. The resulting microparticles were found to be easy to prepare, and they yielded retention and dewatering results competitive with other colloidal silica and bentonite products. Swerin et al. [28] reported the preparation of anionic sols acidifying silicate solutions with either alum or ferric chloride. Again, the
effects on retention and dewatering were comparable to commercial aluminum-treated colloidal silica products. The lab-prepared metallosilicate hydrosols produced improvements in retention and after-press solids when added to a cationic-starch-treated furnish on a high-speed pilot paper machine.

**Silica micro-gels:** A motivation for the development of yet smaller colloidal silica particles was the fact that decreased primary particle size tends to decrease the amount needed to achieve a certain level of drainage improvement in the presence of cationic starch or acrylamide [56]. Geometrical considerations ensure that the specific surface area of smooth, non-porous objects of fixed shape ought to be inversely proportional to their surface area. If this were the only consideration, then one should produce smaller colloidal silica particles to increase their efficiency on a mass basis.

Rushmere [1,115] patented procedures for preparing “polysilicate microgels” by controlled aging of partially acidified silicate solutions. The primary particles were of approximately 1-2 nm diameter [80], leading to surface areas greater than 1000 m²/g [1,3]. Consistent with information provided by Iler [55], such microgels also are reported to contain chains or agglomerates of primary particles. Once the particles have been formed, the mixture is diluted to terminate particle growth and prevent premature gelling [80]. This requirement of a dilution step has a subtle but profound effect on how the technology can be implemented; to avoid shipping a lot of water, the commercial approach involves on-site generation. It was estimated that only 40-50% the mass of silica microgel solids was required in direct replacement of a conventional sol-type colloidal silica [80]. In other respects, the impact of silica micro-gels on retention, drainage, and interactions with other wet-end additives all appear similar in character to effects of other colloidal silica products.

**Use of gel-containing silicas:** Though the sol form of colloidal silica seems to be well suited for use with cationic starch, products containing gel-type silica particles, i.e. “structured” colloidal silica, have come into common use for retention and drainage programs involving cationic copolymers of acrylamide [3,83,116]. Advances in twin-wire paper machines, especially those running low basis-weight paper products, have increased the need for retention systems capable of resisting high levels of hydrodynamic shear, and the acrylamide-based microparticle programs with structured colloidal silica appear to offer this resistance [3,117].

To explain why gel-type, structured colloidal silica might be advantageous in some situations, it was observed that various microparticles differ in both charge density and size [96]. Charge density – related to surface area – tended to control the amount of cationic polymer needed to achieve maximum retention, whereas the magnitude of that maximum depended on the maximum dimension of the solid material. Elongated structures yielded higher retention.

**Bentonite** (alkali montmorillonite)

Commercial montmorillonite, or “bentonite” particles are ideally about 1 nm thick by about 300 nm across the plate surface [118]. The effective thickness is often higher, due to incomplete delamination, which is also called “exfoliation.” As was shown in Fig. 1, montmorillonite particles could hardly be more different in shape from colloidal silica. Properties that the two types of microparticle hold in common are high negative surface charge and high surface area per unit mass [118]. Deposits of montmorillonite differ in...
composition and quality, so papermaking grades require careful source selection. Also, the material must be in its “alkali form” to be effective. In other words, calcium or magnesium ions at the particle surfaces need to be replaced by sodium or potassium ions so that the microparticles will swell greatly in water and delaminate, exposing their potentially high surface area.

Bentonite products can be delivered to paper mills as dry powder, but users often prefer to handle liquid formulations, which can be easily pumped and metered. Also, it would make logical sense to predisperse montmorillonite to give it the best chance to become fully swollen and delaminated. However, a highly swollen bentonite slurry contains large quantities of water [118-119]. To reduce the amount of water required for shipping, one approach is to disperse the bentonite initially in an electrolyte solution of sufficient concentration to suppress swelling, and then dilute the mixture before use to allow the particles to swell and delaminate [120]. This approach is said to allow shipping of the product at solids up to 30%.

Some early reported uses of bentonite products in papermaking were associated with water clarification and efforts to remove colloidal material from mill process water [8,48]. For example, Brecht and Dalpke [8] reported significant reductions in biological oxygen demand (BOD) upon addition of bentonite to papermaking furnish in combination with an anionic acrylamide retention aid copolymer. In principle, the high specific surface area of swollen bentonite products, in the presence of flocculating agents, offers a way to remove undesired colloidal material from a papermaking furnish and retain it in the paper [104].

Auhorn and Melzer mentioned the sequential use of bentonite and a cationic polymer as early as 1979 [8]. Ironically, these authors observed a decrease, not an increase in dewatering rates when the bentonite treatment was followed by polyethylenimine (PEI). Bentonite addition followed by a highly cationic polymer also can be effective for pitch control [121].

**Early retention and drainage systems based on bentonite:** The earliest reported uses of montmorillonite for retention or drainage promotion employed non-ionic or low-charge anionic polyacrylamide [47,49,76,122]. Recipes in which the microparticle was added specifically before [47] or after [76] the high-mass soluble polymer have been claimed. A study showed that the strength of interaction between the microparticle and polymer is favored by the presence of calcium ions, to provide cationic sites on the mineral, and by a low charge density of the anionic polymer [122].

One of the patents cited in the previous paragraph describes the possibility of replacing the acrylamide copolymer with polyethylene oxide (PEO) [49]. PEO is a completely nonionic, water-soluble polymer with its own fascinating history of use as a retention aid [89,123-124]. There is no complete consensus of how PEO works as a retention aid. However it is widely agreed that PEO requires a “cofactor” such as phenolic resin or lignin byproducts to work well as a retention aid [123-124]. In this sense it appears that montmorillonite is acting in the role of cofactor when it is added sequentially with PEO, and maybe even when it is used with nonionic PAM.

**Cationic floculant followed by bentonite:** In 1986 Langley and Litchfield described what was to become the second major microparticle program [6]. A high-mass cationic acrylamide copolymer is added first, followed by hydrodynamic shear, and finally by a well-dispersed alkali montmorillonite [26,125]. The system was noted for
offering retention and drainage benefits over a wide range of pH, and it has become widely used for many paper grades [10,26].

Though the most widely used strategy calls for initial addition of cationic flocculant, followed by shear, and then the bentonite [6,10,15,21,26-27,67,72,125-129], other strategies have been considered. For instance Lorz and coworkers [130] claimed a process in which bentonite is added to thick stock, high-charge density polymer is added after stock dilution, and then the stock is treated with flocculant.

**Hectorite:** Montmorillonite is not the only smectite clay mineral that has been considered for use in a microparticle retention and drainage program. Hectorite has been described as a swellable clay with particle thickness typically 100 to 500 nm, and the widths of the platelets are typically 2.5 to 5 µm. Drainage and retention results similar to colloidal silica or montmorillonite have been reported when hectorite is used in combination with cationic starch [69].

**Micro-polymers**

As paper technologists began to understand various attributes and potential of microparticle systems based on colloidal silica and bentonite, one of the questions that they began to ask was “Do the particles have to be inorganic?” It is even worth asking whether the material needs to be particulate in nature. For example, a 1992 patent by Begala describes addition of a high-mass cationic polymer, followed by hydrodynamic shear, and then followed by an anionic polymer in the preferred intermediate molecular mass range of 75,000 to 1,250,000 g/mole [43]. Though the main emphasis of that study appeared to be retention, it is intriguing that Britt Jar test results suggested more rapid drainage. Follow-up work described drainage and retention benefits resulting from an analogous recipe that involved use of an anionic polymer having sulfonate groups [30,131]. Such groups would be expected to make the system perform well down to low values of pH. In another variation, the same type of intermediate-mass anionic polymer was preceded by first a cationic coagulant, then a high-mass anionic flocculant [132].

**A “micropolymer” system emerges:** The best-known micropolymer-based retention and drainage system involves a highly cross-linked, highly anionic polymer known as a “water-soluble filamentary micronetwork” [90]. The polymeric microparticles used in this type of program have been described as between 30 nm and 90 nm in diameter, three-dimensional, and halo-shaped [35,90]. It is worth noting that the same research group reported similar drainage and retention benefits when the described micropolymers were replaced by solid microlatex; however work with the microlatex was not pursued due to processing difficulties [90]. Treatment of the stock with high-mass cationic acrylamide copolymer, followed by this anionic “micropolymer” was found to offer high efficiency, in terms of the amount of the anionic component that had to be added [23,56]. The high efficiency, relative to various inorganic microparticles [12], was attributed to the nearly complete accessibility of charged groups on a polyelectrolyte having an open structure.

**Lignin-based microparticles**

At first mention, the idea seems preposterous – add some lignin-based material back into the papermaking furnish. After all, isn’t that the same material that papermakers work so hard to remove during kraft pulping and brownstock washing?
However, under certain conditions such addition can yield improved drainage or formation \[13,29,81,96,133\]. The additive program described in the cited articles starts in a very similar way to others already mentioned in this chapter, i.e. with the addition of a high-mass cationic acrylamide copolymer, or similar material. The second additive has been described as a modified lignosulfate [96].

If lignin can work, why not a lignin substitute? Lignin can be described roughly as a condensate product of phenolic material \[134\]. It develops an anionic charge in paper mill water due to the presence of sulfonic and carboxylic acid groups. It was found that a condensate product of formaldehyde and naphthalene sulfonic acid salt [135] or phenol sulfone [31] can have similar potential as a microparticle. The latter condensates, described as “tanning agents,” promoted drainage, retention, and a small scale of fiber flocculation when added to stock that had been treated with a cationic flocculant and hydrodynamic shear. A claimed advantage of one of these systems was that it worked with a lower molecular mass cationic flocculant, compared to previously disclosed systems [135].

**Alum-based microparticles**

Aluminum sulfate, or “papermakers alum” has been used as a dewatering aid since the early days of commercial papermaking [136]. The high positive valence of aluminum species, especially under acidic papermaking conditions, makes it an effective agent for the neutralization of negative colloidal surfaces and anionic polyelectrolytes in a papermaking furnish. It is also well known that alum can have colloidal properties, especially if it is added to a neutral or weakly alkaline aqueous solution with strong agitation [16].

Polyaluminum chloride (PAC) products have been noted for the similarity of some of their effects to microparticle systems [77]. Since PAC tends to produce a positive charge on colloidal material, even under typical conditions alkaline papermaking, the effect has been attributed to an interaction with phosphate groups in cationic potato starch [77].

The strategy behind the best-known alum-based microparticle technology is to form microparticles “in situ” in the furnish. The furnish must be alkaline, ideally with a pH near 8 [71]. To form the in-situ microparticles, alum or polyaluminum chloride (PAC) is added after a set of pressure-screens. The optimum composition has been found to contain approximately three OH groups per Al atom, corresponding to the stoichiometry of neutral Al(OH)₃ [62,71].

A puzzling feature of these in-situ-prepared microparticles is their reported negative surface charge under the common pH conditions of alkaline papermaking [17]. There is an apparent disagreement with the expected isoelectric pH of about 9 for pure Al(OH)₃. A possible explanation is contained in the work of Öhman and Wågberg [137]. These authors showed that the isoelectric point of silica sols can be shifted to lower pH values in the presence of various multivalent anions, including phosphate. Phosphates are common dispersing agents for ground calcium carbonate, which was being used as a filler in some of the reported work [17,62]. Earlier work showed that sulfates, another common ion in paper machine water systems, also has a similar ability to lower the isoelectric point of aluminum hydrous oxide precipitates [138].
The system based on cationic potato starch followed by alum has been found to yield maximum retention near to pH=8 in pilot paper machine trials [20]. Both retention and percent solids after the wet press increased with increasing levels of alum addition after the starch treatment.

**Cationic microparticles**

In the list of “defining characteristics” of microparticle programs near the beginning of this chapter there was a suggestion that the particles ordinarily ought to be strongly negative in charge. But how about a positive charge? In principle the mechanisms still could be valid, but one would expect such particles to be suited to systems using a high-mass anionic acrylamide copolymer as the main flocculant. Since papermaking furnish generally enters the paper machine system with a negative zeta potential, there ought to be some potential savings to be achieved by using a kind of microparticle that does not need the furnish to be shifted to the cationic side for it to have its best effectiveness [53].

**Cationic aluminum-based microparticles:** Already in the preceding section on “Alum-Based Microparticles” it was necessary to invoke the presence of phosphate ions to explain how the particles could have a negative charge at a pH of 8. Not surprisingly, other researchers have used related methods to prepare aluminum-based microparticles of net positive character [54]. These authors described their particles as “fibrous” and having mean particle sizes in the range 167 to 1490 nm. These particles were found to work well in systems that had been treated with high-mass anionic acrylamide flocculant of low charge density. The process worked best at very low pH, consistent with the expected increasing positive charge of aluminum species with decreasing pH. However the system was said to be tolerant of a wide range of pH, as used by papermakers.

Polyaluminum chloride (PAC) itself usually is not considered to be a microparticle, but it may be worth making an exception in some cases where PAC is the last additive to a paper machine. Such a scenario is involved in a patent by Smith [44]. The claimed process involves four steps. First, one adds a high-charge cationic material, the coagulant. Next, one adds a high-mass anionic polymer. Third, one applies shear to break fiber-to-fiber attachments. And finally, one adds the PAC. As in the case of the in-situ aluminum-based microparticles described earlier [62,71], it was proposed that the aluminum additive had polymerized or associated in-situ to reach colloidal dimensions [44]. Though the patent lists 1-1000 nm as the range of size of the microparticles created during the papermaking operation, it is reasonable to expect PAC also to simultaneously form complexes with anionic polymer chains. Though there may be some debate as to whether the claimed strategy actually involves microparticles, the results in terms of retention and drainage appear similar.

**Cationic microparticles formed by charge reversal:** Let’s first consider various work aimed at converting the surface charge or existing microparticles from anionic to cationic [139-142]. Though it is well known that charged polymers, multivalent ions, and even surfactants can reverse the surface charge of particles, it does not necessarily follow that a stable colloidal suspension results. Subtleties of mixing sequences, agitation, or selection of materials may spell the difference between a stringy precipitate and a cationic, opaque colloidal dispersion.
In view of the discussion in the preceding section on Aluminum-Based Microparticles it should come as no surprise that aluminum chemistry could be used to coat the surfaces of negatively charged microparticles and render them cationic. For example, colloidal silica particles can be coated with aluminum oxide [139]. Compared to other inorganic oxide surfaces, aluminum oxide has a relatively high isoelectric pH [143]. The cationic charge of hydrated Al₂O₃ persists up to a pH of about 9. Moore [140] achieved a similar result by treating silica sols with boric acid-stabilized basic aluminum acetate or formate to prepare cationic colloidal silica. Alternatively, the colloidal silica could be mixed with aluminum chloride solution, heated, and then treated with base [141]. Svending [144] claimed a process in which the cationic microparticles were added in combination with cationic polymers.

**Charge reversal of microparticles by polyelectrolyte adsorption:** In principle one even can adjust the charge of microparticles by the adsorption of water-soluble polyelectrolytes. For instance Derrick [145] patented the use of low to moderate-mass cationic or anionic polymers to adjust the zeta potential of microparticles to an ideal level. One would expect that charge reversal by this approach would be costly, because of the high surface area and charge of colloidal silica. Even in the cited work, the treated particles were reported still to be negative in zeta potential.

**Cationic latex:** Intriguing experiments were carried out by Ono and Deng [146], who showed that cationic micro-latex could be used effectively as part of a retention aid system. Interactions among the cationic latex, anionic acrylamide copolymers, fibers, and calcium carbonate filler appeared to be controlled by charge interactions and by a form of polymer bridging. It is worth noting that the procedure used in this cited work differed from most common microparticle programs in the following respects: (a) the cationic micro-latex was added *before* the flocculant, whereas typical microparticles are added after a flocculant and hydrodynamic shear; and (b) no drainage benefits were claimed. The field appears open for further work in these areas.

**“Other” microparticles**

Another indication of success of microparticle technology consists of the number of inventive ways in which people have attempted to copy it. One such approach involves hydrolyzed titanylsulfate [147]. Such particles were found to work with cationic starch to give good retention results over a wide pH range.

Conventional calcium carbonate particles used in papermaking tend to be much too big (0.5 – 4 µm) and insufficiently negative in charge to be considered as possible substitutes for, say, colloidal silica or bentonite in a microparticle program. But Gill and Sanders [70] showed, in principle, that both of these problems can be overcome. A colloidal precipitated calcium carbonate (PCC) sol, made highly anionic by adsorption of phosphate ions, was found to be effective for retention and strength, when used in combination with cationic potato starch.

Though most developers of microparticles have aimed for high absolute values of surface charge and zeta potential, there is at least one report of work with the opposite approach [148]. The negative zeta potential of colloidal silica was reduced by treatment with a silane coupling agent. There was no report of how such treatment affected retention and drainage.
If all else fails, one might even employ a mixture of known high-performing microparticles. One such patent involves cationic starch treatment, followed by bentonite and colloidal silica, either sequentially or as a mixture of the microparticles [149]. Premixing of a cationic acrylamide copolymer with bentonite also has been proposed [78]. Until more is known, neither of these approaches appears to achieve sufficient advantages in performance to compensate for the added complexity.

POLYMERS USED WITH MICROPARTICLES

In light of the wide use of terms such as “microparticle programs” it is possible that the polymers used with microparticles might get insufficient attention. Colloidal silica and bentonite have become well known to papermakers only in the past 10 to 20 years, whereas cationic starch and cationic acrylamide copolymers have been used for much longer. One might argue that the polymeric components of microparticle systems ought to receive at least equal mention for the following reason. Microparticles have almost no effect when added to untreated pulp. By contrast, the polymeric flocculants are used commonly as stand-alone additives for retention, dry-strength, stabilization of size-emulsions, and so forth.

The subject of cationic starch has been reviewed [150-151]. Likewise, there have been good descriptions of acrylamide copolymer retention aids [100,152]. Therefore, this review will mostly limit itself to aspects of these polyelectrolytes most related to their use with microparticle systems.

Cationic starches and guar

As already noted, cationic starch use in microparticle programs mostly has been associated with the use of colloidal silica sols [5,14,85,101,153]. In the early years the starch component almost always was cationic potato starch. More recently other cationic starch types, especially corn starch products, have come into use. Most of the cationic starch used in these systems has been of conventional charge density and with no effort to change the as-received molecular mass. Charge densities in the range 0.2 to 0.3 percent nitrogen (or a degree of substitution up to about 0.04) have been favored, at least in part, because the Food and Drug Administration (FDA) allows use of such products in all grades of paper. Potato starch is sometimes considered a premium starch for microparticle programs because of the relatively high molecular mass of its linear, amylose component [154].

One might anticipate that there ought to be a performance difference if one were to compare cationic starch products based on amyllopectin (branched starch, very high molecular mass) versus amylose (linear starch). Though most potato, corn, and other sources of starch used by papermakers supply a mixture of the two types, papermakers have the option of selecting waxy maize products that have almost 100% of the branched form. Laboratory tests suggest that either pure form of cationic starch can separately perform very well as part of a retention and drainage program with colloidal silica; however the amyllopectin appears to have the stronger reaction with microparticles [19].

Higher-than-usual charge cationic starch products have been proposed for various applications in furnish with relatively high cationic demand [79,85-86,94,117,153]. It is worth noting that high-charge cationic starches also may help achieve retention and
drainage effects in mill systems with relatively high electrical conductivity of process water [155]; work is needed to show that this remains true when microparticles are being used.

A high molecular mass usually is considered desirable when preparing cationic starch for use in a microparticle program. One approach is to avoid degradation of the starch mass before or during its cationization [156] or during its cooking [2]. Another approach has been to cross-link the cationic starch to increase its effective molecular mass [86,103]. High-viscosity cationic starch has been found to improve the drainage and retention performance, when followed by either bentonite or colloidal silica in the laboratory or commercial applications.

To improve the dry strength of paper, cationic guar gum has been claimed as a preferred treatment, when followed by colloidal silica [102]. Though papermakers most often think of cationic starch products when they want to improve dry strength, sometimes they turn to guar products when they need something even more effective on a mass basis. Guar products supposedly earn their reputation as superior bonding agents through their very high mass, linear structure, and a superior ability to adsorb onto fibers and other carbohydrates because of a chain structure that matches that of cellulose [157].

**Cationic acrylamide copolymers (cPAM)**

Cationic acrylamide copolymers (cPAM) with molecular masses in the range of about 4 to about 15 million grams per mole have become the most commonly used flocculant component of microparticle systems, even including those involving colloidal silica [2-3,6,10,11,13,21,23-24,31,56,61,72,93,95-96,131,133,158-161]. Most literature references stress a need for high molecular mass of the cationic flocculant to be used in microparticle programs; in patent literature this is often expressed in terms of intrinsic viscosity. In some cases the mass-average molecular mass can be as high as 20 million grams per mole [133]. Charge densities up to 10% are common, and again this limit may be more related to FDA rules, rather than any inherent advantage of 10% charge. According to Krogerus [162] relatively high-charge cPAM products used with bentonite outperformed low-charge cPAMs for promotion of dewatering in lab studies. However, the low-charge cPAM systems gave better first-pass retention. The growth in popularity of cPAM products for microparticle systems is no-doubt related to their very high potency as flocculants, making them well suited to application on large, high-speed paper machines, especially on twin-wire formers [117]. According to Aloi [35], higher-mass, higher-branched cPAM flocculants may be needed for faster paper machines.

As discussed earlier in this chapter, achieving highly uniform formation is often a prime motivating factor in a paper company’s decision to use a microparticle program in place of conventional retention and drainage treatments. However, as we have seen, the cationic starch and especially the cationic acrylamide copolymers used in most of these applications initially have the effect of increasing fiber-to-fiber flocculation. Though these flocs are assumed to be mostly broken down as the furnish passes through pressure screens or other high-shear zones in the paper machine approach system, the situation causes one to ask, “Shouldn’t there be a way to achieve the same benefits without having to initially overflocculate the stock?” According to Shin and coworkers [37] the answer is “yes,” particularly if one treats the stock with a certain class of highly branched cationic polymers. The polymers were designed in such a way that they were unable to
adopt flat conformations on surfaces to which they become adsorbed, and in this respect they have something in common with high-mass cationic flocculants. However, in the latter case the tendency to maintain loops and tails may be partly attributed to the slowness of conformational changes [36]. The highly branched cationic polymers did not by themselves produce significant fiber flocculation, but flocs resulted after the interaction with colloidal silica. Follow-up work will be needed to determine whether the system is promising in terms of retention and drainage. A branched polyacrylamide also has been proposed for use with bentonite [82]. There also is precedent for the use of lower-mass cationic polymers in combination with microparticles to avoid overflocculation of stock [163].

**Anionic acrylamide copolymers (aPAM)**

Though cationic high-mass polymers get most of the attention in discussions of microparticle systems, there are two contrasting roles played by high-mass anionic flocculants.

The first option involves conventional, anionic microparticles. It has been discovered that useful effects can be achieved by a sequence of high-charge, moderate-mass cationic copolymer, followed by high-mass anionic copolymer and colloidal silica or bentonite [42,74,76,164]. In some mills the microparticle has been added in the same stream with the anionic flocculant. Clues to the mechanism come from the facts that (a) the colloidal silica and anionic flocculant do not form any complex with each other in the absence of other additives or furnish, and (b) the moderate-mass cationic additive, followed by colloidal silica are not sufficient by themselves to give a strong drainage improvement.

The second option involving aPAM copolymers involves cationic microparticles [1,44,54]. Again, the furnish is first treated with a highly cationic additive to provide anchoring sites for the flocculant. Additives that may play the role of microparticle in such situations would include soluble aluminum compounds [44], pre-formed aluminum-based microparticles [1,54], or possibly micro-latex [146], though the latter scenario has not yet been reported.

**MECHANISTIC ASPECTS OF MICROPARTICLE SYSTEMS**

Uses of specific microparticle programs and applications will be considered in the remaining chapters of this book, but there seem to be some common features with respect to “how these programs work.” This section will consider mechanistic aspects of microparticle programs in general, weighing evidence for and against various concepts. In principle, an understanding of the mechanisms may make it easier to optimize and control additive flows in a microparticle system. Also there may be clues in the mechanisms that can lead to future developments.

**Electrostatic effects**

Even before the emergence of microparticle programs there has been a lively debate over how significant a role is played by surface charges and zeta potentials with respect to retention and drainage phenomena [165-166]. On the one hand, it has been relatively easy to show a dominant effect of surface charges when one is using a high-charge cationic additive such as a polyamine, polyethylenimine (PEI), or alum...
Maximum drainage, and even maximum retention are often associated with an addition rate that achieves an average zeta potential near to zero. This is not necessarily so when one is dealing mainly with high-mass flocculants [167]. Apparently, charge neutralization can be much less important in some cases where very long polymer chains are able to bridge between adjacent surfaces.

So how do microparticle programs fit into this debate, if at all? Microparticle systems seem to be profoundly affected by charge [2,58,61,98,169]. For example, a charge-dependent mechanism helps explain why the effectiveness of microparticles for drainage promotion seems to increase with increasing surface area (or decreasing size of the primary particles) [2,20]. In cases where the issue has been studied, optimum performance of microparticle programs has approximately coincided with a neutralization of colloidal charges [2,170]. Also, in agreement with classical theories of charge-dependent coagulation, it has been found that increasing salt addition tends to broaden the range of additive ratios over which a maximum interaction can be obtained between a cationic polymer and a microparticle [19]. Often it has been found that excess dissolved polymeric or colloidal anionic materials need to be neutralized with alum or high-charge cationic polymers before a microparticle program can be effective [2,11,23,127,160], or the charge density of the cationic flocculant [79,85] or its dosage [95] has to be increased.

To make matters a bit more complicated, fiber flocculation studies suggest that charge may dominate interactions involving small colloidal silica particles, but that interactions involving the larger bentonite particles may be less charge-dependent [171]. In one study charge issues tended to dominate interactions between a highly charged cationic polymer and colloidal silica, but different results were obtained when the pH was raised to reduce the effective charge density of the polymer [108]. Similar results were achieved in a related study in which the charge density of the cationic flocculant was varied by chemical composition [172].

A “drawbridge” concept

The concept of polymeric bridging is already well established as a mechanism of flocculation by polymers [173], but evidence suggests that microparticles form bridges of a different nature. Differences show up in various studies focusing on such aspects as shear resistance, particle size, particle structure, and reversibility of flocculation after redispersal by strong hydrodynamic shear forces. To help distinguish these differences, the word “drawbridge” will be used in this chapter to designate systems in which microparticles help in the process of flocculating systems that have been treated by a high-mass polymer and the word “bridging” will be used for systems in which there is no additive that plays the role of microparticle.

According to Ford [127], if a retention aid is added ahead of a pressure screen, one can expect hydrodynamic shear to detach some fines from fibers, but others will stay attached to fibers. This situation follows from the observation that the greater shear stress is required for detachment of fine particles, compared to that required to detach fibers or larger particles [174-176]. The word “supercoagulation” was coined to describe how the detached fines could be reflocculated upon addition of a microparticle such as bentonite [127]. The combined effects of the surviving polymer bridges and the drawbridges formed with the help of the microparticles can, in one sense, reverse some of the disruption caused by shear.
These two types of bridges are contrasted in Figs. 2 and 3. As shown in Fig. 2, breakage of an ordinary bridge is expected to be at least partly irreversible. In other words, breakage of the initial bridges is expected to harm the ability of the polyelectrolytes to function again as flocculating agents.

![Schematic Illustration](image)

**Fig. 2.** Schematic illustration of how the molecular mass of flocculating polymer may decrease when bridges are broken in the presence of hydrodynamic shear

A more critical mechanistic question involves how the resulting flocs respond to shear after all components of a microparticle system have been added. A microparticle system ought to be considered somewhat reversible if, after being disrupted by hydrodynamic shear, the fibers come together again to a greater extent than they would have in the absence of treatment [177-178]. Such an outcome would be consistent with the idealized mechanism illustrated in Fig. 3. At least one study failed to find greater reversibility when microparticle programs were compared to cationic flocculant treatment alone [162]. The idea that flocs formed by microparticle programs have relatively high “reversibility” has been verified [60,170,177], though after sufficiently high shear even microparticle programs may fail to show high levels of reversibility [170]. It has been suggested that reversibility of microparticle-induced drawbridges can promote formation of a porous sheet and good fines retention due to sticking collisions when the fibers ultimately come together on the forming fabric or fabrics [16]. It is worth noting that this is essentially the same mechanism that has been used to explain why unstable colloidal suspensions form sediments of low packing density [179].
Fig. 3. Schematic illustration of how unbreakable microparticles can function in a reversible “drawbridge” mechanism of flocculation

Some, but not all investigators have presented evidence that drawbridges formed by microparticle programs are more shear-resistant than those initially formed by a cationic acrylamide copolymer earlier in the same operation. For instance Alfano and coworkers [158] reported that treatment with cPAM alone yielded fiber flocs that decayed rapidly with shear. Subsequent addition of colloidal silica yielded “shear-resistant” flocs, having a slower relative rate of decay of flocculation. By contrast, some others have reported that the microparticle-induced flocs break down more easily in the presence of shear [22], or noted similar shear-resistance [170-171].

Effect of shear on the bridging flocculants: If one follows a typical microparticle application through the process, the polymeric bridges formed by a cationic starch or cPAM flocculant are partly broken as the stock passes though a pressure screen [6,42,45]. As was illustrated schematically in Fig. 2, such treatment can be expected to reduce the flocculant’s molecular mass before the microparticles are added [180-181]. It may be assumed that the rupture of polymeric bridges can leave a preponderance of “tails” of polymers extending from the adjacent surfaces. Work already described involving highly branched cationic polymers suggests that such a situation may be advantageous for microparticle applications [37]; however, more study is needed to clarify this part of the mechanism.

Size effects: A drawbridge mechanism also is consistent with an observed increase in flocculation effectiveness or increased first-pass retention effects with increasing particle size of microparticles [2,182]. Below a critical size of about 3 to 5 nm, silica microparticles yielded less flocculation in the presence of cationic starch [2]. Montmorillonite, due to its high width to thickness ratio, would be expected to have a high bridging tendency. Consistent with this expectation, Mueller et al. [183] found that
the polymeric flocculants had a dominant effect on the extent of flocculation in most of the microparticle systems they tested with colloidal silica, whereas the microparticle had a dominant effect on flocculation when cationic acrylamide copolymer was followed by bentonite. Both optical and rheological studies also revealed strong fiber flocs resulting from bentonite addition to stock pretreated with cationic flocculant [184].

**Molecular-mass dependency:** Ordinarily one expects that polymer bridging effects should be strongly dependent on polyelectrolyte molecular mass [185]. Recent work by Burgess *et al.* confirmed this expectation, but only in the absence of microparticles [186]. In systems to which microparticles were added there was a greater relative effect of charge densities. One reason to expect higher-mass cationic polyelectrolytes to be more effective is that it takes longer for them to adopt a flat adsorbed conformation; within the short time periods associated with the paper forming process it is expected that loops and tails of very long cationic flocculant molecules remain extended out from the surfaces of solids in a papermaking furnish [36]. Evidence in favor of this mechanism includes a reported benefit of furnish pretreatment with high-charge cationics [11,36,129,187]. Though part of the benefit of high-charge cationics might be attributable to neutralization of excess polymeric and colloidal anionic materials [2,11,127,160], the idea here is that partial coverage of surfaces makes it more difficult for a high-mass cationic flocculant to lie down even if there are still sufficient anionic sites remaining for adsorption to take place. Such a “site-blocking” mechanism is illustrated in Fig. 4.

**Fig. 4.** Illustration of how partial coverage of fibers with high-charge cationic polymer may cause cationic flocculant molecules to adopt a more extended adsorbed conformation
**Relative affinities:** The order of addition of microparticles and other additives ought to make a profound difference, according to fundamental work carried out by Åsselman and coworkers [158,188-189]. Coagulation rate studies showed that montmorillonite formed very strong bonds with chains of cationic polymers extending from fiber surfaces. However, the opposite approach did not appear to work well. Addition of the cationic acrylamide copolymers first to the montmorillonite did not allow it later to adhere well to cellulose. Results were interpreted in terms of a high affinity of the polymer for the highly anionic mineral surfaces, causing the polymer chains to lie down flat. The conventional approach of adding cationic polymer to first to fiber is believed to give a greater likelihood that tails of polymer remain extended from the surface. Related work, using simplified collision-rate calculations [36], supports an assumption that cationic flocculant molecules adsorb very rapidly onto fiber surfaces, but that such polymers then are likely to redistribute partly onto energetically preferred adsorption sites on filler or bentonite particles [190].

**Three-dimensional “structure” required?:** A question that needs fundamental study is why there seems to be special advantage in the use of either flocculants or microparticles having a branched structure. It is worth noting that the original silica-based technology involved cationic potato starch, a product that has a high content of branched amylopectin molecules, and these interacted with non-structured colloidal silica sol particles [3,83]. By contrast, some more recent recipes use linear cationic acrylamide copolymers, but these are paired with “structured” colloidal silica products (gels) in which the primary particles are joined together in chains or clusters [2-3,117]. It has been suggested that three-dimensional microparticles should be an advantage, since they cannot lie flat against a fiber surface, and hence they remain more effective for bridging between the microscopically rough surfaces of fibers [38]. The demonstrated high effectiveness of anionic “filamentary micronetwork” or “molecular sieve” polymers in the role of microparticles [56] proves that the microparticle need not be solid. It is worth noting that solid latex particles of related composition yielded similar effects [90]. It has been suggested that, to be effective after application of shear, the microparticle must have a solid-like three-dimensional nature and an ability to avoid being torn apart when adjacent polymer bridges are broken [16,56,71].

**De-swelling of adsorbed polyelectrolyte coils:** Previous work suggests that swollen polymers, including hemicellulose, offer significant resistance to the dewatering process, and it is unclear whether conventional, high-charge cationic drainage aids can reduce the swelling of these hydrogels [34,168]. Swollen coils of cationic starch or other retention aid polymers are thought have the same effect. As illustrated in Fig. 5, the very small size of microparticles, especially in the case of colloidal silica, suggests that these materials are able to penetrate into the coiled structure of adsorbed cationic starch or acrylamide copolymers [2]. Then, one might assume, the complexes formed between the polymer coils and the microparticle would cause the material to contract and expel water [11]. Though this explanation is consistent with increased dewatering and higher wet-press solids [21,25-26,28,39,75,92], it is more difficult to obtain direct evidence. One piece of supporting evidence for this mechanism is an increased density of polymer flocs in fiber-free systems after addition of microparticles [19,186]. There is a need, however, for more direct measurement and quantification of this effect.
Fig. 5. Schematic illustration of proposed deswelling mechanism when small microparticles interact with existing polymer bridges or adsorbed polymer

OPTIMIZATION AND CONTROL

Today’s papermakers who are implementing microparticle programs have a great advantage over the pioneers who made the first attempts in the early 1980’s. First, they have the knowledge that many others have been successful [10-13,23]. Second, the pioneers have cleared useful paths and left some helpful hints. While other chapters in this book will go into more specific detail about specific microparticle program applications, emphasis here will be on some strategies that appear to work in general over a range of microparticle types.

<table>
<thead>
<tr>
<th>Step in Additive Program</th>
<th>Reason for Step</th>
<th>Control Strategies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pretreat furnish with a high-charge cationic additive.</td>
<td>Avoid neutralization of cationic flocculant and/or partly block surface sites.</td>
<td>Monitor dissolved and colloidal anionic substances by charge titration.</td>
</tr>
<tr>
<td>2. Add high-mass cationic flocculant.</td>
<td>Promote retention and provide sites for microparticle attachment.</td>
<td>• Dosage (tray solids test) • Molecular mass • Charge density</td>
</tr>
<tr>
<td>3. Apply hydrodynamic shear.</td>
<td>Break fiber-to-fiber flocs for uniform formation and good vacuum dewatering.</td>
<td>Select flocculant addition point, usually before screens or before fan pump.</td>
</tr>
<tr>
<td>4. Add microparticle.</td>
<td>Promote water release and compensate for bad effect of shear on fines retention.</td>
<td>• Dosage • Particle type</td>
</tr>
</tbody>
</table>
Table 2 lists some basic steps of a typical (but not universal) microparticle program. As shown, each of the steps can involve some sort of optimization.

**Step 1:** Referring to Step 1 of Table 2, the usual recommended strategy is to add just enough of the highly cationic material to neutralize most of the anionic colloidal material, while still leaving sufficient anionic sites on the fiber surface so that a cationic flocculant can adsorb efficiently. Spence [191] described a way to determine this optimum dosage level by using a special streaming potential titration procedure. For routine testing and for online monitoring it is more usual to directly titrate the white water or filtrate from the headbox to a streaming potential of zero [192-193]. More stable operations are expected if the cationic demand prior to flocculant addition is kept at a selected target value [88]. Fiber-pad streaming potential tests seem to be the next most promising type of online sensing method for charge [22,57,194], but most papermakers are still relatively unfamiliar with such methods.

**Step 2:** When one wants to control the overall retention response of a microparticle system, it is most common to adjust the dosage of the high-mass flocculant [15,67]. In practice this is best achieved with online monitoring and control of tray-water solids [24,88,93]. A possible alternative approach involves online floc size monitoring, especially if there is a good correlation between a floc index and retention [158]. Typical dosage levels of cationic acrylamide copolymers are expected to be in the range of about 0.05 to 0.1% on a solids basis [23].

**Step 3:** About the only way that papermakers can practically adjust the level of hydrodynamic shear after flocculant addition is to select the addition point. On a typical paper machine there are relatively few options to choose between. The most common choice is just ahead of a pressure screen or screens [6]. Post-screen addition strategies risk an excessive level of fiber flocs in the product, though some of these flocs can be broken as stock passes though a hydraulic headbox [46]. Addition of flocculant at an earlier stages of the process can make sense on relatively slow paper machines [21].

**Step 4:** Though microparticle dosage clearly is important, it is a common practice to leave the flow of microparticle at a constant level during a production cycle [15]. This approach tends to simplify the control strategy. On the other hand, once excess colloidal charge has been controlled there is usually an optimum ratio of the flocculant and microparticle [20,171]. More sophisticated control strategies are likely to be common used in the future.

**Charge balance and addition rates:** Charge considerations have been found to be critical for establishing the most effective relative amounts of cationic and anionic components of a microparticle system [2,6,14,22,79,171]. In many cases it has been found necessary to optimize neutralization of excess anionic dissolved and colloidal substances, using such additives as alum or polyaluminum chloride (PAC) [23,25,99], polyamines [10], or high-charge cationic starch [79,153]. In fact, it has been suggested that best results can be achieved if the net amount of cationic polymers is something of an overdose, reversing the original zeta potential [22]. Due to these requirements, one should expect a higher overall requirement of cationic polymers compared to a typical retention and drainage program that does not use microparticles [189]. These considerations tend to make microparticle systems somewhat more expensive and dependent on process sensors and adjustments to keep them working well. In return for
these efforts, microparticle systems also appear to be somewhat more tolerant of increased salt levels, compared to conventional retention aid systems [14].

**Selection of microparticle type and shape:** By selecting a microparticle with larger size or more chaining or agglomeration of primary particles it is possible to shift the benefits more toward retention benefits and away from an exclusive concentration on drainage and formation [2]. Faster paper machines and twin-wire machines may call for the use of higher-mass, higher-branched flocculant polymers and/or structured microparticles [35].

**TRENDS AND NEEDS FOR THE FUTURE**

Twenty years ago few papermakers could foresee the upcoming growth and impact of microparticle technology. In retrospect, the developments have come in response to needs for increased production rate and quality. So, one of the first places to look, in asking about the future of microparticles, is at the present needs of papermakers. According to Main [11], advances in paper machine design are tending to decrease the importance of drainage promotion. Rather, the high hydrodynamic shear of modern hydraulic headboxes and twin-wire formers place more critical requirements on achieving acceptable first-pass retention while still maintaining good formation [128].

**Strength:** Another future emphasis is likely to be on paper strength. Users of low-quality, low-freeness waste paper can use microparticle treatment strategies both as a way of achieving acceptable drainage and as a way of increasing the practical amount of wet-end starch [75]. It is ironic that the earliest technology resembling a modern microparticle system was described as a binder system [107], and that a similar emphasis might again predominate in the future.

**Lab test development:** Every long-term papermaker will have heard the phrase “you can’t observe these benefits in lab tests; you have to run it on the machine to see the benefits.” Indeed, conventional freeness tests, etc. sometimes fail to show the benefits of a microparticle program [96]. Due to a lack of water recirculation in some common lab methods it may be necessary to add 4 to 5 times the usual dosage of some additives [85]. To help minimize the lost production and expense of mill trials, there is a need for dynamic tests that better emulate the conditions of shear, pulsating flows, and vacuum application that are inherent in paper forming processes [10]. Much progress already has been achieved [162,195-196]. However, evaluation of microparticle programs, especially at the mill, could benefit from further advances in lab testing.

**LITERATURE CITED**


