

FILLER RETENTION - RECENT CHALLENGES AND POSSIBLE SOLUTIONS.

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Abstract

The need for increased filler content coincides with increasingly complicated paper machine wet-end chemistry. Certain paper sheet properties and economics of filler application depend not only on the amount of filler retained, but also on the way it is distributed in the sheet. Low retention, over-flocculation, two-sidedness of filler distribution all can affect brightness, opacity, gloss, strength, dusting and other important quality aspects. Problems in filler retention can also lead to serious operational problems like deposits, breaks, and holes.

This paper will look at the recent challenges related to filler retention through the eyes of a wet-end chemist. We will discuss sources of retention problems for various type of fillers and formulate some strategies for stabilization of paper machine operations. Factors such as pH, conductivity, cationic demand will be considered. Importance of an on-line control and monitoring strategies of retention and factors that affect it, will be discussed. Some innovative ways of application of retention additives will be introduced.

Retention Mechanisms

Cationic retention aid are generally polymeric additives which function through fine particle aggregation and heteroaggregation of fines and fillers.[1-7] The mechanisms which comprise these processes include adsorption of the additive to the surfaces of fines, fillers, and fibers, the neutralization of charge on the surfaces of particles by formation of cationic patches, and the agglomeration of fine particles through electrostatic attraction of oppositely charged particle surfaces or through particle bridging flocculation by high molecular weight, cationic additives. Each of these steps is dependent upon the charge density of the polymeric additive used, the conformation of the additive, the charge density of the particle surfaces. The dependence on surface charge and polymer configuration is the source of the role water chemistry plays in the performance of retention aids.

Water Chemistry

The effect of water chemistry can be summarized by examining pH, conductivity, and dissolved and colloidal substances (DCS). The charge density on the surface of fines, fibers and fillers is determined by the acidity of functional groups on these surfaces. In many cases, the charge determining groups are carboxylate groups. Since the pKa value of carboxylic acid is approximately 5, the degree of ionization of this group changes drastically over the pH range of 4 to 6; this coincides with the pH of acid papermaking. As the pH increases, more carboxylic acid groups ionize and the charge density increases. This is true for the fibers, fines, dispersants and for DCS in the furnish. Unquaternized polymeric amines used as retention aids simultaneously lose some of cationic charge at pH values above 6.5-7. The changing charge density or charge demand suggests that varying pH will have a strong effect on the interaction of cationic retention aids with furnish components. The unpublished data from one of our trials in a Canadian SC mill using TMP furnish with delaminated clay and an on-line retention program control with Kajaani RM200 showed that the change of pH between 4.8 and 5.6 resulted in an increase of flocculant flow by 40% to maintain constant white water consistency. Recent work at one of the Canadian SC mills showed that the change in pH from 4.8 to 7.3, that would accompany the neutral pH conversion, results in the cationic demand change from 850 $\mu\text{Eq/L}$ to 1700 $\mu\text{Eq/L}$.

The interaction of retention additives with fiber, fines, filler and DCS in a furnish is a surface effect; that is, it involves the interaction of the solubilized cationic additive with functional groups on the surface of the

furnish particles. Any furnish characteristic which influences the form of the surface functionalities or the conformation of the additive in solution will effect the performance of the additive. Conductivity and DCS concentration will effect both the form of the surface groups and the conformation of the retention additive. The conductivity of a pulp suspension is the result of the fresh water chemistry, combined with the types and quantities of additives from anywhere in the process, and the degree of closure of the mill water system. Increasing conductivity affects the furnish components by shielding the charged groups on one surface from charged groups on another surface. This will allow agglomeration to occur in the absence of charge neutralization by cationic additives. The shielding effect also changes the conformation of charged additives. In the case of a highly charged polyelectrolyte, an increase in conductivity will shield intramolecular charged (cationic or anionic) groups from one another, allowing the polymer to adopt a more collapsed conformation. Since the effectiveness of the polymer is based upon its interaction with a surface, the decrease in size will reduce the effectiveness of the polymer. In the case of flocculants this effect is particularly clear, in that the role of flocculants as bridging molecules requires them to be as voluminous as possible to maximize the bridging effect. The effect of conductivity mainly results from charge screening, and is not based upon chemical or solubility changes of the additives.

The effect of DCS, specifically with cationic polymers, is based upon chemical changes due to complexation. DCS is made up of various dissolved and colloidal substances resulting from the wood pulping and bleaching processes[8]. These substances are “detrimental” based upon the effect they have on cationic retention additives. By this definition, these substances are oligomeric, polymeric or colloidal in nature, and, will generally carry an anionic charge. These substances come from the production of high yield, mechanical pulps. The detrimental substances originate from alkaline conditions, such as practiced in peroxide bleaching. The cationic charge demand, a convenient measure of DCS concentration, is determined by titrating the DCS with a soluble cationic polymer (*e.g.*, poly(diallyldimethylammonium chloride)) to an isoelectric point detected with a color dye [9] or with a streaming current detector [10], off- or on-line. The number of equivalents of cationic polymer consumed corresponds to the amount of anionic trash in the sample. The typical levels of DCS as measured by colloidal titration with streaming current indicator are listed in papers by Gratton [11] and Ojala [10]. These detrimental substances, or anionic trash, complex cationic retention aids with different results. Lower molecular weight, high charge density retention aids react with DCS with the result of neutralizing the charge demand of the DCS. This is the basis for the use of charge demand titration to estimate the concentration of anionic trash in a pulp suspension. The presence of DCS has a similar effect on the higher molecular weight, lower charge density flocculants; complexes between trash and flocculants prevent the flocculants from adsorbing to particles in the furnish. Effective use of cationic retention chemicals typically involves the addition of a source of cationic charge (*e.g.*, alum, cationic polyelectrolytes, cationic starch) to reduce the charge demand of the pulp suspension. The lower concentration of anionic trash allows the subsequent use of a cationic flocculant.

Filler Differences Affecting Retention

Effective filler retention provides the quality benefit that the papermaker expects or a more cost-effective sheet, if filler cheaper than the fiber source is applied [12,13, 14, 15, 16] . Benefits of filler application have to be balanced against their deleterious effects - paper strength reduction and increased retention requirements being most important. It is therefore very important to understand the differences of retention characteristics between the fillers and to choose retention programs and strategy providing maximum benefits of filler application at the lowest filler level. For instance, in order to achieve smoothness, a different z-direction retention is required than if opacity is the goal. Total retention is not necessarily indicative of successful retention either. With titanium dioxide retention, the most benefit from this filler will be realized if it is retained without agglomeration of the individual particles.

The most important characteristics of the filler impacting its retention properties are:

- particle size, shape and surface area
- surface chemistry
- surface charge

Fillers are retained by the mixture of mechanical entrapment of original filler particles or their agglomerates and heteroflocculation with other components of the furnish: fines or fibers. If the mechanical entrapment dominates, when retention aid is ineffective or is not used, filler particles are simply trapped in the pores of formed web of paper. In this case retention obviously increases with the particle size of the filler. Fillers that have a plate-like character are retained better than more symmetrical filler particles. In general, coarse fillers are retained better, while the finer fraction accumulates in white water systems. When mechanical entrapment is a dominant filler retention mechanism, the produced sheet exhibits some level of two-sidedness in filler concentration. This phenomenon is particularly evident for sheets produced on Fourdrinier-type formers.

Chemically, the most important industrially fillers are: kaolins (various forms of hydrous aluminum silicate), calcium carbonates (GCC, PCC, chalk), and TiO_2 (rutile, anatase). The differences in the chemical nature of the surface of the filler particle has a large impact on the adsorption property of the retention aid. This impacts the bridging flocculation mechanism. It is well known that polyacrylamide based flocculants adsorb well to the kaolin clay particles and polyethylene oxide (PEO) does not adsorb well onto PCC surfaces. Another consequence of the chemical nature of filler is its surface charge or ζ -potential. ζ -Potential is best determined from electrokinetic measurements. The value of ζ -potential may be directly related to the chemistry of filler particle surface or may be a result of surface modification, for example, the addition of a dispersant. Various fillers display different affinities to water. Clays (hydrous, calcined) and calcium carbonates are hydrophilic, while titanium dioxide, talc and sodium aluminosilicate are hydrophobic. Hydrophobic fillers, generally, require dispersants to form stable slurries. Dispersants significantly change surface properties and ζ -potential of the filler.

The extent of planning, product selection and experience required to achieve successful filler retention is reflected in the number of parameters which control filler retention, combined with the importance of retaining the filler in a manner providing the desired sheet quality effect.

Monitoring and Managing Anionic Trash

Anionic trash, or detrimental substances, are named based upon their effect upon retention programs. The degree to which a retention program is affected by anionic trash is dependent upon the concentration of anionic trash in a pulp suspension. The measurement of charge demand by complexation titration is now commonly practiced in the industry. The following examples illustrate the relationship between trash concentration (as measured by complexation titration) and retention.

In the first study, samples were taken from the high bright thick stock line of a Midwestern mill producing a light-weight coated grade. The samples were filtered, and the charge demand of the DCS was measured by complexation with poly(DADMAC) using a streaming potential endpoint. Samples were collected over time and correlated with retention data from the machine. The variation in machine retention follows the changes in charge demand (FIGURE 1). In another example [17], the addition of a twin-belt press for thickening peroxide-bleached pulp to 30% consistency had a significant effect on the amount of retention chemicals used, and, more importantly, the variability of the retention (Table 1).

	Twin roll press 'On'	Twin roll press 'Off'
COD (ppm O ₂)	1500 - 2000	3500 - 4000
Cationic Demand (µeq/L)	1200 - 1700	2500 - 2700
Conductivity (mS/cm)	0.7	1.9
Cost of retention	60%	100%

Table 1 summarizes the effect that pressing peroxide-bleached pulp has on wet-end chemistry and retention aid consumption.

In another example at a Canadian newsprint mill, on-line measurements of charge demand were compared to the on-line retention measurements. In this case, as in the last case, the on-line retention measurement controlled retention aid feed-rates. The data from the trial (FIGURE 2) illustrate the effect charge demand has on retention aid demand, which reflects retention aid performance.

One of the ways of increasing the levels and economics of filler retention is to modify the filler slurry before is being injected to the furnish. This strategy can be based on two separate approaches. One, based on pre-flocculation of filler leads to an increase of the particle size of the filler and increases the contribution of mechanical entrapment in the overall retention of filler. The impact of such pre-agglomeration on sheet properties has to be well monitored. Pre-agglomeration of filler may lead to losses in opacity, brightness and increased levels of filler two-sidedness. Losses in opacity will be especially evident if TiO₂ was pre-agglomerated - leading to reduction of light scattering TiO₂-cellulose interfaces. On the other hand, if the changes in optical properties are acceptable, filler pre-agglomeration should result in a stronger sheet. The second approach in filler pretreatment is based on non-flocculating modification of the surface of the filler in such a way that improves its later interaction with the main dosage of retention polymer. The most typical example of this type of approach is treating filler slurry with a low dosage of coagulant. It is often done by feeding coagulant to the dilution water of the filler. An example of such application is described in the recent paper by Tomney, *et al.* [17]. In this paper low dosage of coagulant significantly improved the economics of filler retention with no apparent impact on any of sheet properties monitored during the well designed trial. In general, filler pre-treatment can be a very good way of increasing filler retention as long as relevant sheet properties are closely monitored. Another approach, the white water addition of retention polymers, could be considered a filler specific application as it targets these small particles that by accumulation in the white water streams, proved to be most difficult to be retained.

Summary

It is apparent that increased levels of filler in produced paper, more difficult and varying water chemistry of the papermachine, more frequent changes in the production grade structure and more challenging final sheet quality expectations require a more complex approach to filler retention applications. Selection of proper filler for expected quality benefit, identification and removal of the sources and dynamics of water chemistry changes, on-line monitoring, and on-line control of conditions and performance of the papermachine, will all contribute to increased productivity and consistent sheet quality of the paper. The creative application of retention polymers based upon the understanding of retention mechanisms may contribute to increased economics of filler retention in the mill, as long as final sheet quality is closely monitored.

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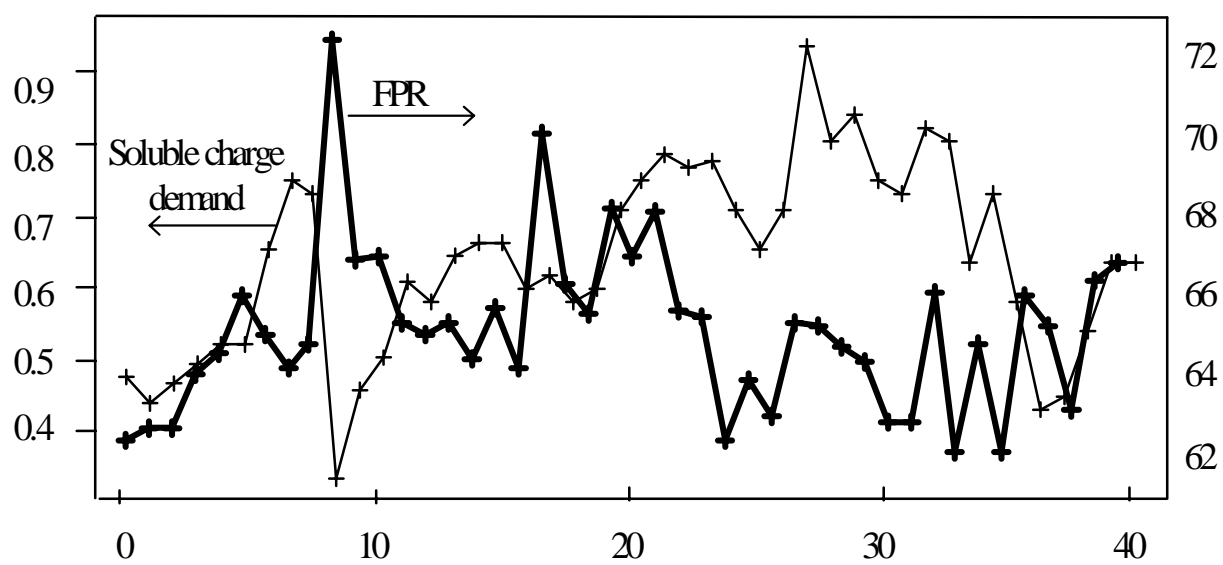


Figure 1 summarizes first pass retention (%) and soluble charge demand (meq/L) trends. These data show that variations in soluble charge demand appear to coincide with fluctuations in first pass retention.

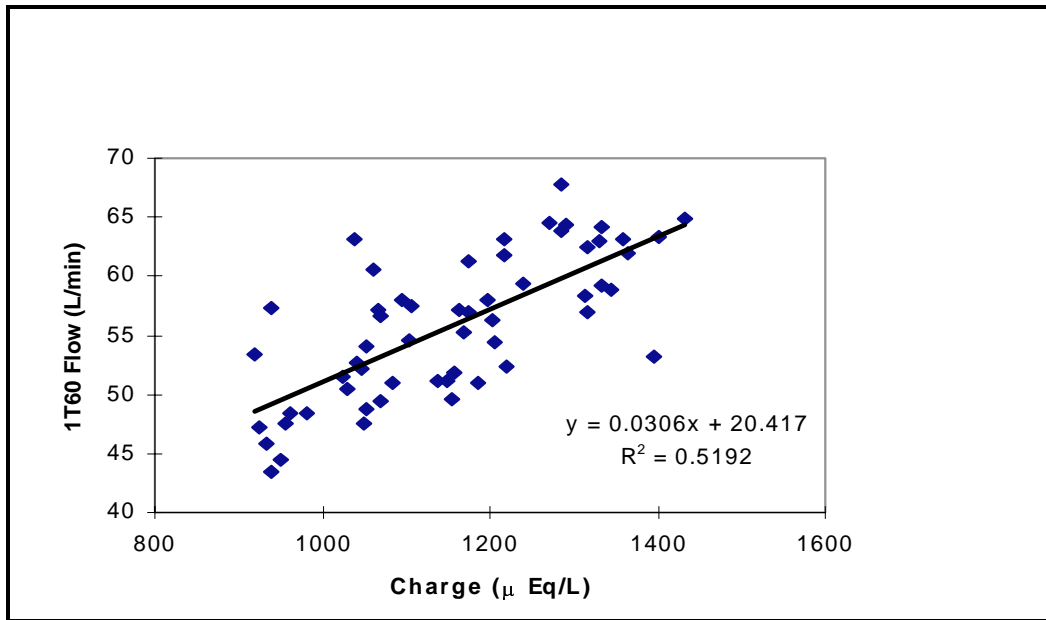


Figure 2 illustrates the effect of changing charge demand (measured on-line) on flocculant (1T60) consumption. The flocculant flow is controlled on-line to maintain constant whitewater consistency.