

Efficient Use of Performance Enhancing Chemicals in Present Scenario

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ABSTRACT

Twenty years ago almost every fine paper maker believed paper had to be made in an acid environment. Only a few specialty products, most tissue, some food board, and corrugating medium were made under alkaline conditions. During past decade many improved chemical formulations were introduced in the market by various chemical manufacturers with better understanding of problems being faced by paper makers globally. This technology advancement not only helped to reduce the sizing cost but improved the total wet end chemistry. Many polymers, Additives, Enzymes, Biocides and Deposit control programmes were tried alone or in combination as per the requirement, which resulted in improved paper quality and smooth run ability of the paper machine. Sizing cost reduced substantially when system switched over from acidic to neutral and finally to alkaline condition.

Keyword: Alkaline paper, AKD sizing, ASA, size reversion, retention, biocide, deposit.

INTRODUCTION

The Indian paper industry consists of 500 mills with mill capacities ranging from less than 1000 t/a to over 100 000 t/a. In 2002, the country's total paper and paperboard capacity amounted to 6.2 million t/a, of which about 5.1 million t/a was registered as operational while the balance 1.1 million t/a was reported as idle capacity.

The industry is highly fragmented. Top five producers account for about 25 % of the capacity. The largest paper companies in India are typically owned by large private industrial conglomerates, or by the state.

The word alkaline is used loosely. A better term would be neutral pH buffered paper. A pH range of 7.0 to 8.5 is generally not considered alkaline, but relative to traditional acid paper making pHs the new conditions are alkaline. It is becoming the new standard as more mills move to alkaline conditions. There are good reasons for converting to alkaline systems, but the change introduces a new set of challenges. The process chemical changes that provide lower fiber costs through fillers and archival permanence also create problems. One challenge is retaining the fillers. Another is controlling slime and deposits. ***Ineffective deposit control will hide the advantages, destroy machine efficiency, and hurt profitability.***

Right Sizing

Sizing specifications are designed, first and foremost, to ensure that paper meets the needs of people who use it.

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Take, for instance, cup stock. Rapid penetration of beverage fluid through the paper tends to defeat the purpose of the cup. Even when liquid packaging has a barrier coating or laminate film, it still makes sense to make the fibers hydrophobic, i.e. "water-hating" to minimize wicking at the seams.

Sometimes a change in how the paper is made means that old sizing specifications get out of date. Assume, for instance, that Paper Machine "A" used to run at a wet-end pH of 5.3 with rosin size and alum. Then a decision was made to produce the same grade with calcium carbonate as the filler. The presence of calcium carbonate typically implies a pH value above 7, favoring a switch from rosin sizing to "alkaline sizing." The best-established alkaline sizing agents are ASA (alkenylsuccinic anhydride) and AKD (alkyl ketene dimer). In a future issue we can consider the choice between the two of them. But let's assume that the mill personnel chose AKD and successfully matched all of the same sizing targets. The mechanism of action of AKD is a bit different from rosin, so it's worth asking in each case whether the sizing test specification, or the test method, needs to be updated. Too much AKD just raises costs and runs the risk of slipperiness or adhesion problems. Too little sizing might cause problems too.

A second group of people who "need" hydrophobic sizing agents are the papermakers themselves. Consider the difficulties of trying to run an unsized sheet through a puddle-type size press. A "soggy" sheet coming out of the size press usually means a high frequency of

web breaks. But let's assume it doesn't break. Extensive re-wetting of paper at a size press or coating station has the potential to make the sheet dimensionally unstable. The resulting cockling and uneven elongation of the sheet can adversely affect performance of the sheet in converting and printing operations. Finally, excessive penetration of size press starch into the sheet can increase the load on the after-section dryers - slowing production in some paper machine systems.

A Purpose for Each Wet-End Chemical

Progress in explaining the environmental consequences of papermaking additives already has been achieved in a series of publications that appeared in the early 1990's. Few chemicals papermakers actually use. If one ignores brand designations, differences in concentration, and minor variations in molecular mass or composition, then only about 200 individual chemicals are commonly added to paper machines, not 3000. The relatively low number of chemical additives used in papermaking is consistent with the fact that this industry mainly makes low-cost, high-volume products; we simply can't afford to use superfluous chemicals.⁽¹⁾

If one were to omit all chemical additives from a papermaking process, then the consequences would include larger increases in emissions of solids, biological oxygen demand, and even of noxious gases - resulting from uncontrolled growth of slime in paper machine systems.

Saving Energy: Let's take a closer look at how wet-end additives can reduce the energy required used in papermaking. Removal of water uses by far the largest component of that energy. Most water is removed by gravity drainage, application of vacuum, inertial effects, and pressing. However, most of the energy is expended during a subsequent process, drying by evaporation⁽³⁻⁴⁾. Approximately 2 to 9 million BTU are required per ton of product, to evaporate water. Substantial savings in energy can be achieved by shifting a greater proportion of the water removal to the preceding unit operations of forming and pressing. One way to accomplish this goal is to accelerate dewatering with chemical additives. There has been much work in this area (5-7). It is generally agreed that each 1% increase in solids content of a paper web should yield about a reduction of 4 to 5% in the net drying load. Pulp mills are often net producers of energy in the form of steam or electricity, but savings in the energy of drying has the potential to either decrease the consumption of fossil fuels or decrease the production of greenhouse gases.

About in terms of additives, Three classes of chemicals stand out as the major drainage chemicals in current use (8-9). These three classes are often called "coagulants," "floculants," and "microparticles." Coagulants used in papermaking are generally multivalent or polymeric compounds of high positive charge density. Commonly used coagulants include aluminum sulfate ("papermakers' alum"), polyamines, and polyethyleneimine (PEI). Floculants complete the process of bringing fine particles together; the most widely used type of floculants in the paper industry are very high mass copolymers of acrylamide. Amounts typically less than 0.05% based on product mass are sufficient to increase the retention of fine particle in paper as it is being formed. Microparticles are tiny negatively charged particles such as colloidal silica, bentonite, or highly branched carboxyl compounds; they interact with cationic polyacrylamides or cationic starch to further promote dewatering (10). A common characteristic of all of these drainage-promoting chemicals is that, to perform their function, they adsorb onto the surface of solids in the papermaking furnish. That means that these chemicals tend to be retained well in the paper; relatively little of it remains in

liquid effluent from paper machines, even before wastewater treatment.

Defoamer chemicals affect many aspects of papermaking, in addition to drainage, but it is the drainage benefits that have the clearest connection with environmental impact. Especially in the case of heavier weights of paper or paperboard, higher levels of fines or bubbles can be expected to clog the drainage channels in a wet sheet of paper⁽¹¹⁻¹²⁾. Defoamers are added to the wet end in the form of emulsions; little droplets of oily material spread rapidly on bubble surfaces and cause the bubbles to coalesce. The result is less entrained air coming out of the headbox. Its improvement in drainage can be converted into dryer paper going into the wet-press section.

Decreasing Effluent Loads: In papermaking is that paper is formed on a relatively coarse, continuous screen fabric; typically the openings in the fabric are large enough so that between about 5 and 50% of the solids delivered to the forming section are capable of passing through those openings. The small particulate material in paper, the "fines," may consist mostly of wood byproducts⁽¹³⁾. Even before it is refined, it is necessary to develop the bonding ability of fibers for most grades of paper, but refining also increases the level of fines in the slurry. But all of these wood-derived fines can be overwhelmed by fine material of a different type, the mineral fillers⁽¹⁴⁾. Calcium carbonate and clay are the major types of fillers used, and they make it possible to achieve opacity targets with less total materials.

To understand how retention aid chemicals can impact the environment it is worthwhile to view papermaking operations as the first step in a multi-step water clarification process. Though there is a great deal of overlap between "retention chemicals" and the fore-mentioned "drainage chemicals," the emphasis of a retention program is to increase the relative proportion of fine materials that stay with the wet paper web as it is being formed⁽¹⁵⁾. The very-high-mass acrylamide copolymers, polyethylene oxide in combination with phenolic cofactors, and also high-mass acrylamides, in combination with microparticles, can be very effective retention systems, even in some cases where the surfaces of the suspended matter are far from being neutral in charge. Higher

retention efficiency implies that less solid material is present in the water that drains from the paper. The traditional name that papermakers used to describe the filtrate water from papermaking is "white water." A generation ago it used to be more common for white water to contain so much clay, titanium dioxide, and air bubbles that it looked like milk. Now, largely thanks to chemical additives, together with screen devices called save-alls, solids levels of white water are kept under control and nearly all of the fine material eventually ends up as paper.

Wet-strength agents: Environmental concerns about wet-strength chemicals are often associated with their monomer composition, possible residual monomers, and the possibility of regenerating these monomers and releasing them into the environment. The traditional wet-strength resins most often used for acidic papermaking conditions are based on formaldehyde⁽¹⁶⁾.

Dyes: Papermaking colorants tend to have relatively poor biodegradability⁽¹⁷⁾. Fortunately there has been a trend towards dyes with relatively high affinity for solid surfaces. That means that the dyes tend to leave the paper machine as part of the product, not in the water to be treated. In addition, dyes entering the wastewater plant tend to be removed with biological sludge. High affinity onto solid surfaces is generally achieved by development and use of relatively large, planar molecules - the so-called "direct" dyes. Affinity for fibers is further promoted by the trend for more use of cationic direct dyes, in cases where these are appropriate⁽¹⁸⁾.

Acrylamide copolymers: Considering their benefits in reducing the waste of unretained fines, it is easy to love retention aids. Copolymers of acrylamide are the most widely used very-high-mass floculants to promote fine-particle retention. On the one hand, acrylamide products are expected to contribute much less to biological demand (BOD), compared to the amounts of starch products needed to render equivalent benefits in terms of either retention or dry strength. On the other hand, they are not easily biodegradable, as is to be expected, based on their molecular mass. The maximum permissible level of monomers present in acrylamide copolymers is 750 ppm, compared to

100 ppm in the case of other polymers. Acrylamide products have received the more lenient limits due to their history of 40 years of use in the paper industry without evidence of harm.

Highly cationic copolymers:

One step towards addressing concerns about possible environmental impacts of highly cationic polymers is to avoid using more than is needed. For instance in the spraying of forming fabrics it is possible to minimize the chemical use by proper dilution and by use of a well-designed spray boom. When used to neutralize excess colloidal charge, it is possible to avoid overdose of highly cationic polymers by carrying out online or laboratory charge titrations with streaming current instruments⁽¹⁹⁻²²⁾. Charge control to the neutral range has the advantage of tending to maximize precipitation of most polymers and fines onto fiber surfaces, reducing the amounts of polymeric and colloidal substances that are sent to the wastewater treatment system.

Recently there is yet another option to consider, the use of highly cationic polymers based on starch or other natural products. Already a highly cationic polymer based on starch has been used for charge neutralization and optimization of wet-end operations. Presumably such materials might be more easily biodegraded, compared to their synthetic counterparts.

Biocides: Conventional slimicides are highly toxic. They have to be to perform their function. Many do not break down readily during treatment of wastewater⁽²³⁾. Enzymes are very good at self-destruction. The fragile nature of enzymes is due to the fact that they consist of complex proteins with many loops and coils that have to fit together in an exact way to perform some kind of function. Even moderate changes in pH or temperature can temporarily or permanently destroy the enzyme's activity. Enzymes such as amylases are already used for cleaning up deposits on starch-preparation equipment and paper machine wet-ends.

Another way to minimize the need for toxic agents to control slime involves biodispersants. Biodispersants make sense because bacteria attached to surfaces, the so-called "sessile" bacteria, tend to cause more problems than freely floating bacteria in paper mill systems. Although it is premature to expect that biodispersants can

eliminate the need for toxic biocides, or of oxidizers such as chlorine dioxide, it is reasonable to expect the dependency on such materials to be reduced.

Starch: Starch products probably wouldn't even be included in the present discussion, but for the fact that the paper industry uses so much of them. The largest proportion of starch is added to the surface of paper at the size press or in coating formulations. Additional starch is commonly added at the wet end in levels up to about 1% on paper mass. Native, underivatized starch is close to ideal in terms of its biodegradability⁽²⁴⁾.

It should come as little surprise that most starch now added at the wet-end of paper machines is either cationic or amphoteric (i.e. having both positive and negative charged groups attached to the chain). The down side is that cationization of starch appears to make it less biodegradable.

Sizing Agents: Internal sizing agents are truly remarkable in their ability to transform the nature of paper, even when the added dosages are typically well below 1% of the dry mass of product. The chemical composition of wood-derived fibers makes them highly water-loving. Paper uses for cups, bags, cartons, and various printing applications can require that it resist water absorption and penetration. Rosin size has been criticized for its toxicity and for the fact that rosin sizing usually requires the use of aluminum compounds. But rosin products can claim a positive attribute not shared by the common alternative sizing agents; rosin is a byproduct of wood pulping. Rosin is a renewable, biodegradable material. There is an interesting balance between rosin's efficiency and its biodegradability; most rosin is reacted with maleic or fumaric anhydride to produce "fortified" rosin size. The fortified size is more storage-stable and more efficient in use. However, it also is less biodegradable than natural rosin.

Though it still is worth considering environmental implications of rosin size products, there has been a strong trend over the past 20 years towards alkaline papermaking conditions and the use of calcium carbonate filler⁽²⁵⁾. Values of pH higher than about 7 make it increasingly harder to size paper with conventional rosin products. Fortunately, two widely used "alkaline sizing agents" are available.

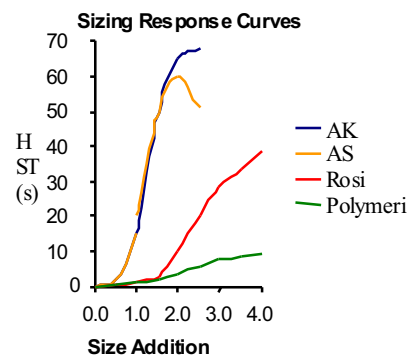
Alkenylsuccinic anhydride (ASA), which is very popular for production of printing papers and gypsum board liner, is a byproduct of petroleum. By contrast, alkylketene dimer (AKD) is made from fatty acids, a renewable resource. In either case, alkaline sizing agents tend to be much more efficient than rosin in terms of the amounts needed to reach equivalent levels of resistance to fluids.

Sizing paper with chemical additives Mechanism

1. It must be uniformly distributed in the stock, inherently hydrophobic or become hydrophobic under use conditions and it must be retained on the fibers.
2. It must be uniformly distributed on fiber surfaces, firmly anchored to fiber surfaces and it must be properly oriented on fiber and filler surfaces.

Sizing Agent Characteristics

Greater hydrophobicity is attainable with synthetic sizes compared to rosin, Polymeric wet end sizes are 'soft' sizing agents. Shown In figure.

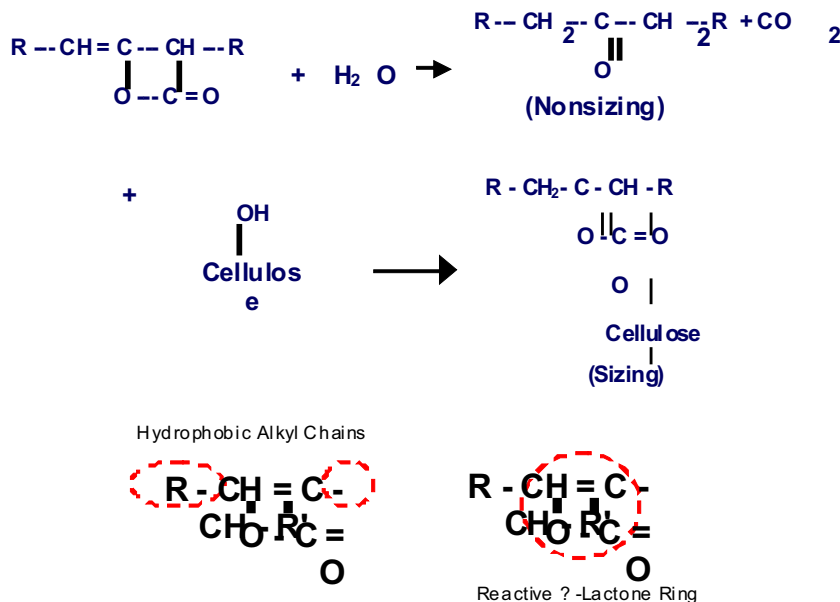


Comparing Sizing Agents

AKD: Generally the hardest possible sizing, but the slowest curing, greater tendency for sizing reversion, potential for slip problems and Low shelf life (1-2 months.)

ASA: It is more tolerant of furnish variations, high temperatures and extremes of pH than other sizes, ASA similar cure rate to rosin, except in Mechanical furnishes and Di-acid can cause deposits, press picking and de-sizing

Reactions & Applications Technology AKD Alkyl Ketene Dimer



Alkylketene dimer (AKD) contains two hydrophobic groups (R) and a lactone group that is capable of reacting with the hydroxyl groups on cellulose. It also reacts with water to produce a waxy solid, which is not an effective size because of poor anchoring to the cellulose.

ADVANTAGES OF CELLULOSE-REACTIVE SIZES (ALKALINE SIZING) OVER ROSIN SIZES (ACID SIZING)

- Use less/no Alum
- Operate at pH > 7
- Ability to size Calcium Carbonate-filled sheets
- Higher sheet strength (or substitute filler for fiber)
- Easier white water reuse
- Reduced/eliminate alum deposits
- Reduced corrosion

Strategies for use

- Because AKD is received at the paper mill as a ready-made, milky emulsion, it can be a very convenient product to use.
- Also, the lower reactivity of AKD, compared to ASA, means that the papermaker has more flexibility on where to add it. For example, many users of AKD add it to the thick stock; this practice tends to get the AKD to the fiber surfaces. In contrast, adding a sizing agent to the diluted furnish in the thin stock loop can be expected to concentrate more of the size onto the fines fraction.
- The presence of precipitated calcium carbonate (PCC) in the

system can reduce the effectiveness of the sizing agent and also it may cause the sizing to lose some of its effect during storage (sizing reversion). Recent work reported by Bud Brungart showed that this effect can be minimized by adding the PCC early in the process.

- Paper made with high levels of AKD is likely to be slippery, and it may cause problems in precision cutting and register during conversion, or in stacking during high-speed xerographic copying.

Retention - Addition Point

- The choice of addition point affects the selectivity of the size for a particular furnish component (e.g.: dosing AKD close to an anionic filler addition would cause the size to be preferentially adsorbed on to the filler instead of the fibres.) Adding a sizing agent to the thick stock maximises its retention on fibres, rather than fines and fillers.
- All sizing agents should be added to streaming stock, immediately before an area of high shear. Whilst not absolutely essential, it is good practice to add the size with carrier water.

Conductivity, pH & Charge Demand effect AKD retention

- High conductivities causes cations to become adsorbed on to the fibres, impairing the retention of cationic functional additives.
- A low pH reduces the dissociation of carboxyl groups on the fibre

surface, lowering the fibre cationic demand, and thus impairing the retention of cationic additives.

- A high cationic demand due to dissolved colloidal materials (Disco, or Anionic Trash) interferes with retention generally, and impairs the retention of cationic functional chemicals specifically, by adsorbing them and neutralising their charge.

Cationic 'Functional' Chemicals

- Generally improve sizing performance by increasing AKD retention *on fibres* (the same mechanism as a 'Cure Promoter,') but this depends on the Charge Demand.
- Alum may impair AKD performance by pH depression and interference from the Al³⁺ ions.

Anionic Additives & 'Process' Chemicals

- Usually impair sizing by a variety of mechanisms (e.g.: Anionic Dyes adsorb size & reduce size retention, Deformers acting as wetting agents, etc.)

Fillers often impair si

- Fillers increase the Spzing performance specific Surface Area of a furnish. Most mineral fillers are naturally hydrophilic.
- Poorer retention of size adsorbed on fillers and Filler morphology affecting the rate of reaction of AKD (e.g.: PCC.)

Distribution

- Adding the size into a region of high shear will distribute it evenly throughout the furnish.
- If the AKD melting point is higher than the temperatures in the Wet End, the AKD will start to melt in the Dryers. (Note: the use of an AKD wax that will undergo re-crystallisation at the temperatures in the Wet End should be avoided.)
- The molten AKD is prevented from spreading whilst the size particles are surrounded by water molecules, due to the high surface tension.
- The AKD spreads on to the fibre surface forming a mono-molecular layer (in theory.) It can also

migrate on to fillers, and especially in the case of PCC, in to the voids of filler agglomerates.

- Migration of unreacted AKD is also possible after drying (e.g.: between the different plies of a sheet.)

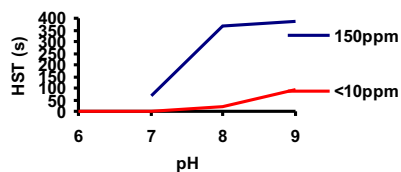
Curing -AKD Reactions

- When AKD reacts with cellulose, the lactone ring is broken, forming an ester linkage with cellulose hydroxyl groups, and orientating the two hydrophobic alkyl chains away from the fibre surface.
- β -keto ester formation was the subject of some controversy, but it was always recognised that two fractions of AKD were present in the sheet: one extractable by solvents for AKD (unbound AKD), the other one unextractable (reacted AKD).
- AKD also reacts with water forming an unstable β -keto acid, which rapidly de-carboxylates to form the ketone. Under alkaline conditions, it is believed that this reaction is faster than the one with cellulose.
- There is no reaction with carbonate fillers, though hydrolysed AKD might form Ca-salts.
- Unreacted AKD can display a weakly hydrophobic character.

Curing - pH & Alkalinity

- AKD sizes are effective over the pH range 6.0-9.0 (7.0-8.5 optimal)
- The reaction with the fibres is catalysed by bicarbonate alkalinity (optimum 150-250ppm, as CaCO₃). GCC (chalk and marble) usually provides sufficient alkalinity. With PCC, the use of NaHCO₃ is recommended as a buffer, to reduce [Ca²⁺], and thus deposits.
- Sizing reversion may occur under conditions of very high alkalinity and pH (especially hydroxide alkalinity.)

AKD Cure Rates



AKD-Deposits: AKD deposits on a paper machine can have different causes:

Dispersion quality: filter plugging & wet end deposits (Ensure the quality of the AKD including storage at the paper mill).

AKD retention: wet-end deposits (Ensure good retention by selecting correct dosing point and charge of the dispersion. Blend with WE starch if possible)

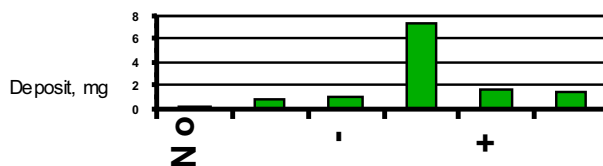
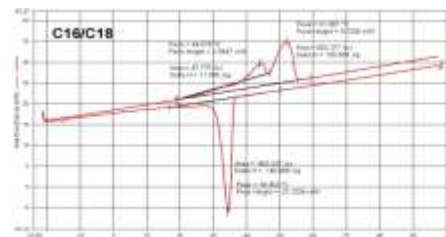
AKD melting point vs. PM temperature profile: wet-end deposits and press-section deposits (Avoid a wax melting point close to the PM wet-end temperature, Avoid "cold spots" in the press-section and Select a different (low mp) AKD dispersion)

ASA Emulsion Hydrolysis Rates

- Water permeates through the protective colloid of the ASA emulsion, causing hydrolysis.
- The rate of hydrolysis is increased by elevated pHs and temperatures.
- The formation of hydrolysate further accelerates the hydrolysis reaction, probably as a result of causing emulsion instability.

Effect of melting point of AKD on deposit formation

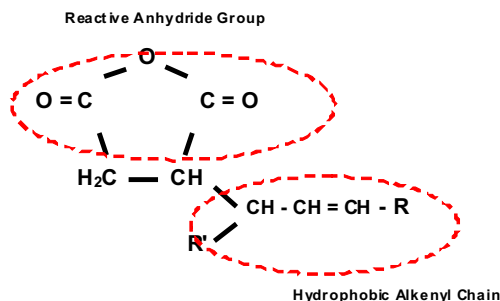
Melting and crystallization point of C16/C18 AKD Wax



Fine paper
Temp. 45 °C
pH 7.5

Melting point of AKD in relation to the process temperature

Alkenyl Succinic Anhydride (ASA)



Applications Technology

- To minimise hydrolysis:
 - >80% first pass retention & >50% ash retention is generally required.
 - Late (thinstock) addition point.
 - Minimise stock contact time.
 - Avoid re-circulation (e.g.: in cleaner systems, etc.)
 - A low dosage of alum to the white water.
- Care with furnish selectivity: Cationic demand, etc.

Alkaline conditions are a favorable environment for microorganisms. Fillers contribute to chemical deposits and scale. Other additives increase the food and improve the substrate for microorganism. The additives themselves form deposits. Secondary fiber increases the challenge. Microorganism and deposit control in alkaline systems takes good process control strategies and financial commitment.

The Move to Alkaline Paper

The transition to alkaline machine systems for fine writing and publication

Traditional Reactive Size Products

Traditional ASA

- * >99% active liquid
- * Long shelf life
- * High reactivity
- * On-machine cure
- * Less sensitive to chemistry fluctuations
- * Alum/PAC etc. aids size retention
- * In mill emulsification required
- * Use cationic starch or polymer to emulsify the product
- * Less affected by size reversion

papers started about twenty years ago. It now has spread to many other products including computer and copy machine grades, magazine, secondary linerboard and even newsprint. In this paper, the term alkaline paper making refers to modern alkaline sized and often coated products. Tissues, corrugating medium, food board and other specialized products have been made under alkaline conditions for years. The concerns of manufacturers of the traditionally alkaline products seem not as great as those of paper makers who are now converting their processes to alkaline conditions. In this paper the focus will be limited to mills making the highly filled publication papers.

Why have mills been switching to alkaline conditions? Some of the reasons being given are valid; others don't hold up in actual practice. Reasons include:

- Improved strength through better fiber bonding. Yet the industry does not require stronger paper. The additional strength allows filling the sheet for lower fiber cost and buffering.
- Reduced corrosion at alkaline conditions. Galvanic corrosion is reduced but a new type of corrosion takes place. The new corrosion destroys the milder forms of steel and can deteriorate 316 stainless steel,
- To reduce product cost. Cost is not lower in many cases. Enough fiber must be replaced with lower cost fillers to off set the additional costs of sizing agents, retention systems, and slime and deposit control. Ash in the sheet must be high; retention must be excellent, and operating efficiencies must be high. Poorly run mills will see an efficiency drop and cost increase. The best run mills will make more money.
- Improved run ability. Requires excellent wet end chemistry and process control. Drainage and formation require good wet end chemistry. Calcium carbonate

Traditional AKD

- * 8% - 20% solids
- * Limited shelf life
- * Low reactivity
- * Off-machine cure
- * More sensitive to chemistry fluctuations
- * Alum/PAC etc. aids size retention
- * Pre emulsified off-site
- * Cationic starch or polymer is used to stabilise the product
- * Affected by size reversion

does not hold water but clay does and can reduce drainage. Deposits and dirt undercut operating efficiencies and quality.

- Improved effluent quality with lower treatment/discharge costs. Seldom is true. Fillers and additives increase effluent loading. Filamentous bacterial bulking in the treatment system can destroy treatment system effectiveness and The market demands it. Customers truly needing archival qualities gain true value with alkaline paper.

In addition there are several reasons not to run an alkaline system. They are:

- Alkaline systems require complex additive dependent wet end chemistry. Good process engineering and additive preservation are needed to benefit from and protect their effectiveness.
- The fillers contribute to a very dirty system. Without high first pass retention the fillers become scale and deposits thus causing poor sheet quality. Coating and broke reuse increase the problem. Fillers also contain sulfates and phosphates that contribute to scale. Filler slurries contribute microbiological contamination.
- AKD and ASA are microorganism nutrients as are cationic starch and emulsion polymer retention aids. All deteriorate to become deposits. Alkaline sizes not retained are quickly hydrolyzed. The hydrolyzate forms a gelatinous deposit that resembles microbiological slime. This slime is a good place for microorganism to grow.
- Alum prevented pitch and stickies deposits in acid paper. Problems from these deposits increase in an alkaline system. Using alum in an alkaline system does not work and causes more deposits and scale. This is also true for polyaluminium chloride (PAC). Aluminum hydroxide scale is

common in secondary fiber systems.

The Alkaline Paper Making Environment And It's Additives

The types of alkaline papers we are discussing contain many additives. These additives are critical to the properties of the paper and reduced product costs. Good additive quality is significant for good slime and deposit control.

The most common alkaline paper additives are calcium carbonate and clay (calcium silicate) fillers. Calcium carbonate buffers the sheet and the system. Fillers such as titanium dioxide, barium sulfate and talc (magnesium silicate) produce special properties. Alkaline sizing agents, ASA (alkenyl succinic anhydride) or AKD (alkylketene dimmer), starch and polymeric retention products form a second group. When used, alum and PAC are part of this group also. The third group contains wet strength resins, deformers, dispersants, cleaning agents, chelating agents and microbiocides.

Members of the fourth group of chemicals are not actually additives but the contaminants and/or residuals of the additives. Waxes and oils, multivalent metals, phosphates and sulfates are common in deposits. These stowaways of process chemistry become significant in microorganism and deposit control. High purity fillers are too expensive for papermaking. Surfactants are common ingredients in additive slurries and specialty chemicals. They impact sizing and retention leading to chemical gel deposits. Iron and manganese, common contaminants of starch, clay and calcium carbonate react with some microbiocides resulting in brightness loss and deactivation of the microbiocides.

Microorganism In A Neutral-To-Alkaline Environment

The microflora population shifts significantly to bacteria in alkaline paper making. Five factors, water, food, oxygen (or the lack of it), temperature, and chemicals that stimulate or inhibit growth influence the microflora growth rate. Alkaline conditions are, generally, less favorable for fungi. Fungi still can grow in an alkaline paper making system, the system pH, coupled with a

generally slower growth rate for fungal organism, and a system of biological dominance, cause the dominant organisms, to be bacteria.

The normal operating temperature for alkaline paper machines often matches the requirements for optimal microorganism growth. In acid systems higher temperatures were used to reduce deposit control costs. Because of the tendency of calcium carbonate to form scale at higher temperatures, and an adverse effect on sizing, high temperature operation is not desirable for alkaline systems.

Oxygen is plentiful in the stock and water at the wet end of a paper machine. There are significant exceptions; the areas under deposits and scale, and dead areas in chests and piping. Here anaerobic conditions exist. Several types of anaerobic bacteria become highly significant in these locations. These organisms survive in aerobic conditions but thrive in an anaerobic environment. They metabolize sulfates producing by-products of hydrogen sulfide and iron sulfide. The additives provide the required food. The scale and deposits provide the anaerobic conditions. These sulfate reducing bacteria become the major source of corrosion of carbon steel and even 316 stainless steel. This type of corrosion is called microbiologically induced corrosion or MIC. Another organism metabolizes iron and forms its own scale. This organism is most common in water systems. It is common to find sulfate reducing bacteria under the iron scale and metal pitting under the sulfate reducing bacteria.

The aerobic bacteria in the system have a generous supply of food. Wood polysaccharides, alkaline size hydrozylate, starch, polymers, waxes and oils, and surfactants all can be metabolized by bacteria. Food supply can not be limited effectively given the chemistry of filled and buffered alkaline paper making.

Unicellular and filamentous bacteria thrive in the aerobic alkaline paper making environment. Seldom are they found in pure cultures. They usually are mixed with chemical deposits, filler sludge, and fiber fines. Filamentous strains that have a slime sheath and also entrap particulate matter are common in troublesome machine deposits. Still unicellular slime forming bacteria do cause their share of problems. All microorganisms that will grow in an

additive are destructive to the additives. In acid systems a common organism is commonly called "pink slime" because of the pink to orange to red color.

In alkaline systems this same organism has been found with a variety of colors including blue.

The Common Scales and Deposits of Alkaline Systems

The majority of deposits in an alkaline system are related to the fillers and/or additives. AKD and ASA size hydrozylate, starch, and polymer gels are common. Their appearance is similar to a microbiological deposit and they are often improperly identified as such. Because these materials are food sources for microorganisms the deposits almost always contain biological activity. The real issue for control is which came first, and often the non-microbiological gel came first. Calcium carbonate, calcium sulfate, and calcium phosphate are common as both deposits and scale. Phosphates enter the system with the clay, calcium carbonate, felt washes, and mill supply water.

Aluminum sulfate (alum) takes on totally different properties in the alkaline environment. It does not remain as alum. Aluminum hydroxide gel or scale is common in alkaline systems. Alum is hard to avoid when using secondary fiber but it is not uncommon to find aluminum deposits in mills using virgin fiber. Polyaluminum chloride provides the benefit of substituting the chloride residual ion for the sulfate ion after the aluminum ion reacts, but the production of aluminum hydroxide is still a problem. Alum, once the great solution of the paper maker has now become a major cause of problems.

A Strategy For A Comprehensive Scale And Deposit Control Program

The previous review should make it obvious that the subjects of microorganism, deposit, and machine corrosion control are all strongly interrelated, and are directly related to machine profitability. Implementing a program of control for just one aspect will not achieve the operating results nor the sheet quality desired. Furthermore, an incomplete comprehensive program may not protect the assets of the corporation.

Machines and systems should be

washed at every opportunity. Although not as thorough and effective as a boil-out, a good wash-up will reduce the accumulations of deposits that nurture microbiological growth, break loose to break the sheet, or cause sheet defects, and reduce productivity.

Alkaline Sizing At The Dry End

Although often considered added operational complexity, popularity of sizing at the dry end of the machine is growing rapidly. Dry end sizing simplifies wet end chemistry and reduces size hydrozylate, one of the major sources and nutrients for microbiological deposit. Sizing efficiency and test results are also dramatically better. Dry end sizing is a major system modification but one that will result in a better product and higher overall operating efficiencies. This investment has good pay back.

Excellent Retention

An excellent retention system is a key element of a good microorganism and deposits control program. Filled alkaline paper contains up to twenty percent material that, without a retention system, is only held in the sheet through mechanical entrapment. The stock to the head box will contain a much higher percentage of filler. Alkaline sizing agents also require a retention system for effectiveness. These additives, along with others, if not retained, soon become deposits, scale and food for microorganisms.

Periodic Boil-Outs For Alkaline Systems

Many managers in mills running acid systems think boil-outs are a waste of production time and do them only on the annual down or when they are absolutely necessary. Such an approach will not work with a filled alkaline system. Periodic boil-outs are an integral part of an alkaline paper making slime and deposit control program. Again, consider the chemistry of the process. Calcium carbonate is added to the system in large quantities. It reacts readily in an acid environment but in neutral-to-slightly-alkaline conditions it is relative non-reactive. The small amount of calcium that disassociates does react with the phosphates, sulfates and silicates to form insoluble scale or deposits. AKD and ASA size hydrozylates are gels that cling to surfaces as do starch and

polymers. Not only are these deposits a threat to productivity themselves but they provide a perfect location for microorganism development. When the deposits first appear they may only marginally impact machine efficiency but as they develop, contaminate the system and come loose; they will cause breaks, papers defects and reduce operating efficiency.

A word of caution, some older mills may have piping and vessels sealed only by the deposits. A first boil-out can be a traumatic experience requiring much maintenance. The alternative is to endure the frustrations, loss of product quality and rapid deterioration of assets associated with a dirty system. The history of the mill is important when planning a boil-out, especially the first one. Slime and deposits are not the only reason for the decline in production with time but they are significant factors. Maximum operating efficiency and profitability are achieved by continuously operating at the top of the curve. A boil-out is an investment. There are real and opportunity costs. It will take time from production and will require chemicals. Not doing a boil-out at the proper time also has a cost, often rather large. Each day machine continues to operate past the intersection of operating efficiency and the efficiency budget, production is lost and average productivity is reduced. Profits that could be made are being lost. Mills that boil-out regularly, at the proper time, make more paper and are more profitable.

For filled alkaline systems two types of boil-outs are needed-caustic based and acid based. A caustic solution with a high concentration of dispersant and chelant should be made up in the pulper to a pH from 11 to 12 and heated to 140° F or higher. Make enough to fill the largest chest in the system. When heated, the solution should be pumped throughout all parts of the system, filling each chest to capacity, and circulating for 2 to 3 hours. The pH will drop with calcium carbonate buffering. Monitoring pH is a good way to gauge the initial amount of caustic to use. Do not neutralize with alum!

The alkaline boil-out will remove organic deposits including pitch, biomass, size hydrozylate and many, but not all, inorganic compounds. A system should be boiled-out with an acid solution at less frequent intervals. Each system will have its own tendency

to form alkaline insoluble scales. **Many mills acid boils prior to an alkaline boil-out every third or fourth cycle.** An acid boil-out should always be done before, not after, the alkaline cycle. Residual acids and calcium carbonate release carbon dioxide and will cause drainage, formation and foam problems for several days. Do not use hydrochloric but most others are acceptable. Bring the solution to a pH between 3 and 4. The acid should be inhibited to protect the metals. Also add an anionic dispersant. There are highly effective dispersants that also inhibit the acid. Acid boil-out can be shorter. One hour to circulation should be adequate. Again, monitoring pH throughout the boil-out is a good method of monitoring needed chemical concentration. If the acid boil-out is not followed by an alkaline boil-out neutralize the acid with an alkaline rinse.

Boil-outs get to the stock wetted parts of the system. Foam guns coat other machine areas with a stable foam coating that will dissolve and disperse deposits. Foam cleaning is excellent for the machine frame, upper parts of chests and catwalks. Always, wash every accessible part of the system once it has been drained. Sludge left in the system causes days of operational and quality problems. The extra time for a thorough wash-up after a boil-out is a must investment.

Do not overlook boil-outs of the additive systems. Clean the sources of system contamination. Consult your chemical supplier for proper procedures for each type of additive system. Safety must be a concern when using strong boil-out solutions. Years ago a steam valve in the wire pit was opened, and flake caustic was dumped on the floor then scooped into the wire pit. A drum of dispersant would be included. Such procedures are no longer acceptable most places in the world. Today suppliers provide premixed boil-out chemistry that is much safer to use. Ask your chemical supplier for recommended chemistry. Know and follow the supplier's safety recommendations.

Finally, inspect the system before starting it up. Look into relatively inaccessible areas. Look for dead spots where scale, deposits, and biomass tend to accumulate. They should be washed and clean. The first inspections may take awhile but once you know the

hard-to-clean areas you can limit the inspection to these. Keep a record of the effectiveness. Dated pictures with a point-and-shoot or Polaroid camera provide a good record.

Chemical Program

The chemistry of slime and deposit control has changed significantly in response to the move to filled alkaline paper making and environmental pressures.

Key points of an effective chemical control program are:

- Minimize contamination of the system. Treat fiber, fresh water, and additives before they reach the machine. Even acid dyes have been found highly contaminated with microorganisms. Treat broke and secondary fiber. If de-inked fiber is used be sure the system is run efficiently.
- Apply chemicals properly. Know which chemical is proper for each situation, how much to use, and how to feed it for maximum effectiveness. There is no all purpose microbiocide. Different chemicals are most effective for different applications. Use a microbiocide appropriate for the environment being treated; pH is the greatest factor. Contact time is another. Chemical interference is a third.
- Analyze the problem properly. For example, alum, size or polymer gels are often mistaken for a microbiological deposit. Also, microbiocides and dispersants are often fed to the wrong locations in the system.
- Use broad spectrum microbiocides where appropriate. There is no sound evidence that organisms adapt to a microbiocide. Other organisms do thrive when the previously dominant organism is controlled. When a highly specific microbiocide is used and eliminates its target population other microorganisms not vulnerable to the microbiocide thrive in the high nutrient environment. Fungal outbreaks are common when selective bactericides are applied improperly.
- Use a biodispersant but use it judiciously. Biodispersants keep microorganisms and particulate matter in suspension and keep

surfaces clean. Misuse can interfere with sizing and retention.

- Monitor the effectiveness of the control program both directly and indirectly. This is so important that it will be discussed in detail in a following section.
- Depend on your chemical representative for technical expertise. A mill's purpose is to make many tons of good quality paper. Today few mills have the technical talent to properly design and control an effective slime and deposit control program, nor of the technical deposit analysis necessary.

CONCLUSIONS

The benefits of alkaline sizing and wet-end controls in today's processes are indisputable. Better automation, ash control, retention and sizing programme, charge monitoring and better biocide programme are the key factors for effective stock preparation management.

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REFERENCES

1. Reinbold, I., "Public No Longer Feels Science and Technology as Something Positive," *Algemeine Papier Rundschau* (APR) 27: 781 (1994).
2. Göttching, L., "Papermaking in Harmony with the Environment," *Proc. EUCEPA Intl. Environ. Symp.*, Paris, pp. 1-25 (1993).
3. Hersh, H. N., "Energy and Materials Flows in the Production of Pulp and Paper," *U.S. Dept. Energy Control Rept. ANL/CNSV 16: 179* (May 1981).
4. Specht, F., "Modern Drying Technologies in Paper and Board Machines," *Wochenbl. Papierfabr.* 120 (23/24):949 (1992).
5. Artama, M., and Nokelainen, J., "Control of Retention and Ash," *Paper Technol.* 38 (8): 33 (1997).
6. Allen, L. H., and Yaraskavitch, I. M., "Effects of Retention and Drainage Aids on Paper Machine Drainage: A Review," *Tappi J.* 74 (7): 79 (1991).
7. Raisanen, K., Karrila, S., and Paulapuro, H., "The Effects of Retention Aids, Drainage Conditions, and Pretreatment of Slurry on High Vacuum Dewatering: A Laboratory Study," *Tappi J.* 78 (4): 140 (1995).
8. Scott, W. E., *Principles of Wet End Chemistry*, TAPPI Press, Atlanta, 1996.
9. McGregor, C., and Knight, P., "Utilizing Process Chemicals to Improve Water Removal," *Paper Technol.* 37 (8): 31 (1996).
10. Andersson, K. and Lindgren, E. "Important Properties of Colloidal Silica in Microparticulate Systems," *Nordic Pulp Paper Res. J.* 11 (1): 15 (1996).
11. Gess, J., "Introduction to the G/W Drainage Retention System," *TAPPI Retention and Drainage Short Course Notes: 49-52* (1989).
12. Gess, J., "The Fines Sensitivity of Papermaking Furnishes," *TAPPI 1991 Adv. Topics Wet-End Chem. Short Course Notes*, 70, 1991.
13. Luuko, K., and Paulapuro, H., "Mechanical Pulp Fines: Effect of Particle Size and Shape," *TAPPI J.* 82 (2): 95 (1999).
14. Bown, R., "Particle Size, Shape and Structure of Paper Fillers and their Effect on Paper Properties," *Paper Technol.* 39 (2): 44 (1998).
15. Gess, J. M., Ed., *Retention of Fines and Fillers during Papermaking*, TAPPI Press, 1998.
16. Spence, G. G., Ed., *Wet- and Dry-Strength Additives - Application, Retention, and Performance*, TAPPI Press, Atlanta, 1999.
17. Wahaab, R. A., "Evaluation of Aerobic Biodegradability of Some Chemical Compounds Commonly Applied in the Paper Industry," *Bull Environ. Contam. Toxicol.* 64: 558 (2000).
18. Jackson A. C. "The Environmental Benefits of Modern Development in Dyestuffs and OBAs," in *The Chemistry of Papermaking*, Conf. Proc. Jan. 27-28, 1993, PIRA, Leatherhead, Surrey, UK, paper 05 (1993).
19. Feng, J., Wei, X., Opalka, A., Pelzer, R., and Schulte, J., "New Generation of Liquid Retention and Drainage Aids," *Wochenbl. Papierfabr.* 129 (1): 32 (2001).
20. Wilhelm, D. K., Makris, S. P., and Banerjee, S., "Signature of Recalcitrant Stickies in Recycled Newsprint Mills," *TAPPI J.* 82 (12): 63 (1999).
21. Phipps, J. S., "Some Mechanistic Insights for Using the Streaming Current Detector to Measure Wet-End Charge," *TAPPI J.* 82 (8): 157 (1999).
22. Gill, R. I. S., "Experience of On-Line Monitoring and Control of Streaming Current at Aylesford Newsprint," *Proc. EU COST Action 14 Workshop*, April 7, Lisbon (2000).
23. Rantala, R., and Koskela, P., "Charge Management on a Woodfree Coated Fine Paper Machine," *Proc. PIRA Conf. Sci. Tech. Adv. Measurement Control Papermaking*, 11-12 Dec. 2000.
24. Chen, J., Hubbe, M. A., and Heitmann, J. A., "Measurement of Colloidal Charge in the Paper Mill by Streaming Current," *Proc. TAPPI 2001 Papermakers Conf.* (2001).
25. Webb, L., "The Chemical Make-Up of Environmentally Sound Papers," in *The Chemistry of Papermaking*, Conf. Proc. Jan. 27-28, 1993, PIRA, Leatherhead, Surrey, UK, paper 04 (1993).