Global Neutral/Alkaline Papermaking Overview

By: Dominic S. Rende, Principal Consultant, Advanced Technologies Nalco, an Ecolab Company

ABSTRACT
Neutral/alkaline papermaking continues to develop and dominate many paper and paperboard market in the Americas and Europe. These global experiences can provide the foundation for neutral/alkaline papermaking practices in the Asia-Pacific markets. Significant advances in functional and process aid chemicals and their application technologies have supported this trend. Commercial neutral/alkaline papermaking conversions using alkenyl succinic anhydride sizes (ASA) are highlighted.

BACKGROUND
Neutral/alkaline papermaking technology has been developing for over 35 years. Modern interest began in the 1950's and from this point to present day there have been many inter-related drivers supporting this trend. The commercial drivers are based on productivity/economic, quality, and environmental improvements. Advances in functional and process aid chemistries have further supported this trend and have allowed for rapid and successful conversions from traditional acid papermaking.

Neutral and alkaline papermaking are, by definition, separate processes when considering the myriad of paper and paperboard grades produced today. However, many industry representatives now consider neutral/alkaline papermaking as a single, non-acid process. Mineral acids are not used and pH is not generally controlled. Papermaker’s alum and other aluminum-based products may be used but they are judiciously used at levels under 0.5%. Headbox pH can range from 6.5 to 8.5. The majority of the packaging papers and paperboards and molded products are manufactured near neutral, at a headbox pH between 6.0-7.5. The majority of the printing and writing papers are manufactured neutral to alkaline using some amount of calcium carbonate filler, at a buffered pH of 7.8-8.2.

The majority of building products manufactured in the Americas and Europe are also manufactured near neutral. Their headbox pH can range from 6.0 to 7.5.

THE INDUSTRY DRIVERS
Early neutral/alkaline papermaking activity in Europe was spurred by the need to reduce water demand, reclaim and reuse secondary fiber, and reduce process abrasiveness promoted by mineral fillers such as china clays. In North America, neutral/alkaline papermaking was driven by the desire to manufacture more permanent paper products and to significantly reduce the total cost of papermaking as papermaking under acid conditions was limited by corrosion, an inability to produce stronger products, and an inability to reuse a significant amount of process water. The Latin American market has mirrored both North America and Europe in the past decade owing to the expanded availability of process and chemical technologies in this geographic region. These same technologies and supporting industries are now available to the Asia-Pacific papermaking markets. The further advantages of neutral/alkaline papermaking versus acidic systems are:

- Improved sheet strength allowing for:
  - Reduction in energy consumption for process water heating, refining and drying
  - Substitution of filler for fiber as increased filler loadings
  - Substitution of recycle fiber for virgin fiber
  - Ability to use calcium carbonates for titanium dioxide and calcined clays
  - Reduction in basis weights for grades marketed on strength characteristics
  - Less deterioration of fiber by residual acids
- Increased productivity related to reduced down-time and maintenance scheduling
- Use of on-site precipitated calcium carbonates and minerals designed for specific paper properties
• Reduced effluent treatment (pH control, lower sulfates, potentially lower solids)
• Improved mechanical and chemical flexibilities

Although these drivers and benefits are not available to every paper and paperboard market, multiple advantages are generally available to every mill operation. The overriding consideration for pursuing neutral/alkaline papermaking is market driven. A fully integrated, bleached virgin printing and writing operation will respond to different drivers than a recycle-based, unbleached packaging paperboard operation. Process changes and chemical program modifications will be required. Our industry experiences in developing these program modifications over the past 35 years provide the foundation for success.

GLOBAL PERSPECTIVE

Converting from acidic papermaking to a more neutral or alkaline process has been the mega technological trend in paper and board mills in the past twenty years. By 1990, alkaline processes produced approximately 20% of the paper and paperboard manufactured in the United States. Today, the percentage exceeds 70% in many North American market segments. European papermaking operations lead all global regions by producing over 50% of their paper and paperboard output by 1990 under neutral/alkaline conditions. The European Community now produces over 80% of their paper and paperboard products under the neutral/alkaline umbrella. The Latin American papermaking operation is estimated to be in excess of 65% neutral/alkaline. Although the Asia-Pacific marketplace is considered early in neutral/alkaline process development, substantial success stories exist and the global conversion experiences are driving growth in this area.

PROCESS CHEMISTRY

The majority of the paper and paperboard products now produced under neutral/alkaline conditions require internal sizing as functioning process control and end use quality aid. Rosin-based sizing compositions may be used to papermaking pH levels approaching 7.5 but still require a significant amount of an aluminum-based product. The synthetic sizes, represented as alkenyl succinic anhydride (ASA) and alkyl or alkenyl ketene dimer (AKD), are routinely used to manufacture the majority of these neutral/alkaline products. The early North American and European neutral/alkaline papermakers sought size supplier involvement throughout the planning process and these same size suppliers were asked to direct and manage all papermaking additives. It was learned that the knowledge base did not reside solely with the size supplier and that multiple industry participants were needed to develop and participate in these conversions and the subsequent quality improvement programs. The suppliers of other functional and process aid chemicals, such as paper machine and water clarification retention and drainage polymers, deposit control aids (microbiological and pitch/stickies), pigments and dyes, strength aids (natural starch and synthetic polymers for both dry strength and wet strength), and defoamers, all have worked to develop cost effective and robust systems supporting neutral/alkaline papermaking.

INTERNAL SIZING PROGRAMS

The global, internal sizing market is still dominated by rosin-based and synthetic formulations represented by ASA and AKD chemistries listed in Table 1. The rosin-based compositions designed for neutral papermaking are rosin-acid dispersions that may be anionic or cationic formulations. However, rosin tolerance to high alkalinity process water that use calcium carbonate fillers is very limited. The synthetic-based ASA and AKD sizes dominate the printing and writing markets and the packaging and building products markets. These chemistries are tolerant of varying operating pH and furnish compositions and are all cationic dispersions (AKD) and emulsions (ASA).

Table 1. SRI International Market Survey of the Internal Sizing Market, 2000 (1999 Data)

<table>
<thead>
<tr>
<th>Category</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>Rosin-based Compositions</td>
<td>54%</td>
</tr>
<tr>
<td>Synthetic (ASA and AKD-based) Compositions</td>
<td>&gt;45%</td>
</tr>
<tr>
<td>Other (to include wax and asphalt) Compositions</td>
<td>&lt;1%</td>
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</tbody>
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We have estimated the global, 2003 consumption of internal sizes to be in excess of 169 million kilograms, defined by geographic region. The North America size demand approximates 38% as seen in Table 2.

Table 2. Global Internal Sizing Market, 2003

<table>
<thead>
<tr>
<th>Region</th>
<th>Percentage</th>
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<tbody>
<tr>
<td>Latin America</td>
<td>5%</td>
</tr>
<tr>
<td>Europe</td>
<td>28%</td>
</tr>
<tr>
<td>Asian Pacific</td>
<td>29%</td>
</tr>
<tr>
<td>North America</td>
<td>38%</td>
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Global sizing market trends include the:
- Neutral/alkaline sizing of packaging paper and paperboard
- Neutral/alkaline sizing of specialty newsprint
- Conversion from AKD to ASA-sizing of printing and writing paper
- Increase in size demand due to increased filler loading, types of fillers used, and amount of recycle used
- Increase in size demand due to productivity increases
- Slow migration to internal sizing practices from surface sizing

There remains a substantial amount of acid-rosin paper and paperboard globally produced. However, neutral/alkaline conversions continue and are now favoring ASA-sizes over neutral rosin or AKD-sizes. This global trend is based on improving supply chain ASA-size availability and a cost-performance advantage for ASA-sizes when used as a process aid and end use quality aid. Advances in ASA-size technology are listed below. Many poor experiences using ASA in the late 1970’s and early 1980’s in North America were resolved through a better understanding and control of ASA-chemistry, in-mill emulsification, and process emphasis on paper machine fine particle retention practices as:
- Product quality and performance improvements
  - Higher monomeric ASA-content (increases to 95+% purity)
  - Higher molecular weight chemistries (up from the nominal C16-olefin based ASA’s)
  - Greater linearity chemistries, less branching
  - Process controlled and integrated make-up and process feed equipment
- Emulsification flexibility (use of liquid starches and synthetic polymers)
  - Improved physical and chemical stability
  - Reduced process deposition
- Paper machine retention improvements (first pass ASA-retention optimization)

ASA-sizes are routinely used in printing and writing papers for improving size press and coating operational efficiencies. ASA-sizes are commercially accepted for end use-based sizing of packaging paper (bag and linerboard) and paperboard products and in building products (gypsumliner and laminates). The main advantages of ASA-sizes versus wax-based AKD-sizes are economic (lower direct sizing costs in many global markets), efficient process control (controllable on-machine and off-machine sizing), and less end-use problems (as related to converting slip through printing processes).

Several examples of commercial conversions from acidic rosin, neutral rosin, or AKD-sizing systems to an ASA-sizing system are discussed in the accompanying presentation and writings to follow.

RETENTION AND DRAINAGE AID PROGRAMS

Paper and paperboard markets that did not routinely use retention and/or drainage aid systems have overwhelming sought there use as a means to improve paper machine operations. The most widely used retention and drainage systems are generically described as single polymer, dual polymer, or polymer plus microparticle programs. These systems may be more complex than used in acid papermaking owing to the absence of very large amounts of buffering alum. However, these same systems can be more robust and offer the flexibility needed to achieve greater papermaking productivity.

Single polymer describes the use of a flocculating polymer applied to the thin stock following the fan pump (or secondary fan pump in some machine systems). These flocculants are generally high molecular weight polymers that can be anionic, nonionic, or cationic. Flocculants function by adsorbing and bridging furnish components. Recent technological advances have supported alkaline papermaking by developing more robust chemistries in terms of molecular weight, polymer geometry, and in the methods of their make-up and delivery systems. Many packaging, newsprint, and building products markets have successfully applied a single polymer program under neutral/alkaline papermaking.

Dual polymer describes the use of a coagulating chemical in combination with a flocculating polymer. The coagulant is designed to neutralize anionic components (soluble, colloidal, and the charge associated with furnish solids). These polymers also adsorb onto furnish components creating ‘patches’ of cationic charge that promote flocculation. While charge neutralization does not appear to be a key mechanism for the performance of coagulants and flocculants at salt concentrations normally found in paper making systems, charge does play a key role in the activity of these chemicals as retention aids. Reduced water usage, increased recycled fiber content, and increased filler loading may cycle-up the ionic nature of the paper machine water necessitating the need for a process coagulant. Common coagulants include aluminum compounds, synthetic low molecular weight polymers, and even cationic starch. Neutral/alkaline conversions in the newsprint and printing and writing paper markets have been aided by the use of dual polymer programs to improve paper machine economics and finished product opticals.
The third retention and drainage system is commonly described as a high performance alternative utilizing microparticles as flocculation nuclei. The resultant floc structure is smaller, more uniform, and robust and the structure can reform following process shear, unlike the conventional programs described earlier. The microparticle program can use cationic starch or synthetic polymers as coagulants and/or flocculants in combination with the microparticulates. The microparticles are specialty pigments generically referred to as colloidal silicas, borosilicates, and bentonite clays. The traditional flocculating polymers can be added before or after a shear point such as the pressure screen. The program is also flexible with respect to where the microparticle is added and depending on the need for paper machine drainage and retention outcomes. This latter program is widely used in the alkaline printing and writing markets.

Many industry representatives have described neutral/alkaline retention and drainage programs as more complex. A strong case can be made supporting this belief. However, the need to achieve greater operational productivity (faster operations, new machine designs, etc.), improved product quality, and cost reduction (higher filler loading and/or use of less expensive fiber sources) have fostered new and innovative methods for promoting paper machine retention and drainage. A single program, with multiple chemical components, may be required to meet production goals under neutral/alkaline papermaking replacing a program based on alum alone.

FILLER PIGMENTS AND DYES

Calcium carbonate has become the primary pigment used in neutral/alkaline papermaking in both Europe and the Americas. China clays were first replaced by ground calcium carbonate (GCC) in Europe and kaolin clays and titanium dioxides (TiO2) were later replaced/reduced by both GCC and precipitated calcium carbonates (PCC) in the Americas. The availability and use of precipitated carbonates expanded rapidly from the late 1980’s to present and their use was fueled by on-site generating plants capable of modifying crystal morphology to meet optimum optical, sizing, and strength properties. The quality and cost of PCC have ultimately defined their successful use.

Fine and ultra-fine GCC’s offer different performance attributes when used as filler and coating components. Most GCC products are supplied as high solids dispersions stabilized with anionic dispersant. GCC products generally do not provide the bulking potential as many PCC products do but may provide significant, regional-based cost advantages. GCC’s may offer less deleterious sizing and strength impacts and may improve productivity if the mill is steam limited (easier drying). A recent trend is to pursue blended fillers, such as PCC and GCC blends, to balance manufacturing and quality considerations.

DEPOSIT CONTROL MICROBIOCIDES

Microbes are capable of growth in all paper machine systems. They form visible deposits that result in sheet defects, holes or even breaks in the web. Microbes are also responsible for performance loss and spoilage of pulp and expensive functional chemicals. This spoilage can lead to strength loss in fibers, formation of odors that result in rejected products, viscosity loss in starch and a variety of other problems. Microbiological growth is considered by most to be greater in neutral/alkaline papermaking.

The switch from acid to alkaline papermaking has resulted in changes in the microflora of the papermaking systems. In acid systems deposits are m. Fresh water contaminants consisting of protozoa, nematodes and filamentous bacteria are often present. When the same machine converts from acid to alkaline, the microflora changes. Fungi may still be present in deposits; however, they do not tend to thrive at the higher pH levels. Filamentous bacteria go from being a minor component in deposits to a major problem. Levels of fresh water treatment that were considered acceptable for an acid machine are not adequate for an alkaline machine. Filamentous bacteria require stringent fresh water oxidant treatment controls and are very difficult to kill. Control in the machine system is possible, however, only certain biocides are effective against these microbes.

When the machine process changes from acid to alkaline the types of biocides that are used also change. For example, methylene bisthiocyanate (MBT) is very effective in acid systems and is good against fungi. At pH 7, however, it breaks down rapidly. Since this is a slow acting biocide, it is no longer a good choice for alkaline systems. In contrast, oxidants teamed with several other non-oxidizers in a program approach have proven very effective. In general, the alkaline systems require more monitoring and system knowledge for complete control.

COMMERCIAL NEUTRAL/ALKALINE CONVERSION EXPERIENCES

Example 1. A recycle-based, high performance linerboard manufacturer was directed to reduce their total cost of operation, avoid a costly pH control upgrade, and reduce alum required to meet impending environmental restrictions. Linerboard is now manufactured on a 2-ply fourdrinier machine operating at 550+ m/
min at basis weights varying from 125-275 g/m\(^2\) from 100% old corrugated cartons (OCC) at pH 6.0-6.5 using cationic dispersed rosin-size. Approximately 10-12 kg/t active alum was required in addition to maintain sizing. A single component, anionic flocculant promoted by alum and 8-10 kg/t cationic starch is used as the paper machine retention and drainage program. Headbox excursions to over 7.0 pH and process sensitivity to 'soaps' and 'waxes' from the OCC caused significant production losses/downgrading to corrugated medium. The mill’s effluent plant uses an anaerobic digestion process that converts sulfates to H\(_2\)S, creating odor and increasing process corrosivity. A conversion to a low alum required process-using ASA-size (headbox pH 6.5-7.2) has significantly reduced operational and environmental pressures as follows:

- Reduced direct internal sizing costs by 20-25%
- Reduced headbox defoamer by minimum 50%
- Reduced direct dye demand by minimum 20%
- Eliminated culling/downgrading due to Cobb-sizing excursions estimated at $450,000 reduced profits
- Avoided a $500,000 sulfuric acid system capital equipment upgrade (and operational safety issues)
- Reduced sulfate loading to effluent plant by 30-40%
- Strength specifications exceeded by 2-6% above standard
- Opens possibility for further process improvements:
  - Eliminating alum and reducing sulfate levels to 50%
  - Allowing mixed office waste use
  - Allowing potential for basis weight reductions of 2-5%
  - Reducing internal starch demand by 25%

**Example 2.** A virgin, bleached kraft printing and writing paper manufacturer was directed to reduce their total cost of operation, improve paper machine runnability, and improve finished paper quality (reduce end-user problems). Uncoated free papers are now manufactured on a flat fourdrinier (with top wire) machine operating at 800+ m/min at basis weights varying from 75-90 g/m\(^2\) at pH 8.2-8.6 using cationic dispersed 1.25 kg/t AKD-wax. A single component, anionic flocculant promoted with 6-9 kg/t cationic starch was used as the paper machine retention and drainage program. Runnability through the size press and through high speed copying equipment (registering slip) was poor. A conversion to ASA-size (plus 2 kg/t alum) followed by a conversion to a microparticle retention and drainage program significantly reduced operational concerns (size press runnability) and eliminated end-use performance problems. A process coagulant, 1 kg/t, is also used when producing high ash alternative grades.

- Reduced direct internal sizing costs by 20-30%
- Reduced daily machine breaks, primarily through the size press, by 50-75%
- Allowed for an additional 2-5% sheet ash (as PCC) on most grades
- Dramatically improved high speed copier performance (as measured by customer complaints)
- Allowed for some flexibility in size press operation (owing to consistent, pre-size press sizing)

**CONCLUSIONS**

Neutral/alkaline papermaking may provide significant economic advantages over acid papermaking and has become, in many global markets, the dominant papermaking process. The manufacture of printing and writing papers pigmented with calcium carbonate is the process of choice dominating North American and European markets. Building and packaging papers and paperboards are also produced under neutral/alkaline conditions and conversions from acid papermaking continue in all global regions. The manufacture of specialty newsprint papers under neutral/alkaline practice is developing.

There are several commercially viable internal sizing, retention and drainage, pigmented fillers and dyes, and deposit control programs supporting neutral/alkaline papermaking. The proper choice of program is dependent on the papermaking operation and end use requirements for the products manufactured.
REFERENCES


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