NEUTRAL pH CONVERSION IN MECHANICAL GRADES – FINE BALANCE OF CHEMICAL AND MECHANICAL CONTRIBUTIONS

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ABSTRACT:

After most alkaline conversions in wood-free grades were completed in the late 1990's, neutral pH conversions in mechanical grades emerged as the next major industry trend. Converting mechanical grades of paper to higher operating pH is in most cases driven by the desire to introduce calcium carbonate based fillers, which offer a number of cost and quality advantages to the papermaker. In addition, higher operational pH is known to increase web strength development, which allows for higher filler loadings and a reduction of expensive Kraft fiber, commonly added to improve wet web and finished product strength. This increased potential for fiber substitution and the resulting reduction in furnish costs were primary drivers for neutral pH conversions in their early stages. Geographical differences in availability and cost between kaolin and calcium carbonate filler explain the regional differences in advancement of converting of mechanical paper grades production to neutral pH.

Neutral pH applications in mechanical grades are defined by the introduction of reactive fillers, which raise the operating pH to a level that can be potentially harmful to brightness development. Successful neutral pH conversions and neutral pH operation require knowledge, technology and cooperation between the papermaker, the filler supplier and the wet-end retention, sizing and microbiological control supplier.

In this paper the focus will be placed on the recent neutral conversions that, contrary to earlier projects driven mainly by economics, require constant attention to the quality benefits. In such conversions a team of mill personnel and the filler supplier would benefit strongly from a partnership with a quality oriented solutions provider. Evans [1] calls for a "holistic approach" to such conversions - from the pulping/bleaching plant to the printing press. We will discuss the most important elements of neutral pH conversions and illustrate how proper chemical program selection and its application may contribute to successful outcome of these important projects.
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INTRODUCTION:

A number of publications, mainly by filler suppliers, describe the principles and benefits of neutral pH conversion [1-4]. To fully realize the inherent quality and cost benefits of neutral pH conversions, a full optimization of wet-end applications is required. Evans [1] recognizes the need for a "holistic" approach to the conversion. For a neutral pH conversion project to be successful, it is not possible to further continue with practices proven under lower pH conditions. It becomes even more important to develop expertise and application strategies (not just products) that are specific to neutral pH operations.

A partnership focused on providing solutions may mean the difference between a successful and failed neutral pH conversion project. Areas where such a focus is required include retention, drainage, their subsequent impact on filler agglomeration and distribution, control and monitoring strategies, deposit control, pH control, anionic trash management, sizing, foam control, lint control and mechanical aspects of machine operations. Special emphasis has to be dedicated to reviewing and avoiding presence of potentially interfering, not compatible, chemical applications [5].

The recent interest in neutral pH conversions is a result of an increasing market demand for higher brightness, opacity and improved printability within the grade. It is no surprise that these quality drivers and the expected overall cost reductions driven by these conversions are of special interest to producers of supercalendered (SC) grades. Many SC grades that are competing with LWC and ULWC for market share can benefit enormously if they are able to improve maintain quality with improving their cost advantage.

. In 2002, 52% of European and just 20% of North American SC paper was produced at neutral or near neutral pH. These numbers do not only reflect increasing use of calcium carbonate as a fresh filler but also explain a need to adjust operating pH due to the increasing presence of this filler in the recycled furnish. Calcium carbonate in these grades is most often applied in various combinations with traditional, platy

Table 1: Basic sheet quality specifications of various supercalendered grades of paper – from SCC to SCA^{+}.

	SCA/SCA+	SCB	SCC
Basis weight (g/m2)	40-60	49-56	45-52
Filler content (%)	25-40	10-35	0-10
Brightness (%)	67-75	65-70	62-65
Opacity (%)	90-93	92-93	92-95
PPS Roughness (mm)	0.9-1.2	1.3-.1.8	1.8-2.5
Gloss (Hunter, %)	45-55	30-45	25-35

kaolin fillers. The table below presents the main attributes of various SC grades.

Newsprint machines utilizing 100%, or significant amounts, of recycled fiber (RCF) switched to neutral pH to accommodate increasing amounts of calcium carbonates originating from the deinking raw material. Originally, this pH change did not necessitate adding a virgin (primary) source of calcium carbonate filler, although it often happened later to help satisfy the need for improved sheet quality (opacity, brightness, print-through, etc.).

There is a vast amount of information available on the selection of different calcium carbonate fillers, their properties and the impact on sheet properties [2,3,4,6]. In this paper we will not focus on this topic, leaving the decision about selection of the best filler for a given application to the papermaker and filler supplier. We will limit ourselves to the basic information relevant to issues discussed in this paper. There are two major types of calcium carbonate fillers:

- Natural (GCC or ground calcium carbonate) – obtained by grinding various natural calcium carbonate minerals – chalk, marble, limestone, etc. These materials are supplied to the mill in dry form or, in most cases, as high solids slurry, using anionic dispersants.
- Synthetic (PCC or precipitated calcium carbonate) – obtained by precipitation of calcium carbonate from lime and carbon dioxide. PCC can be produced at the mill site as slurry with no dispersant necessary. PCC suppliers offer a variety of PCC products varying in brightness, particle size, surface area and particle morphology. Each of these products offers a different impact on such sheet properties as brightness, opacity, strength, bulk, gloss, etc.

New developments include Surface Modified Carbonates (SMC) [6] where modification of calcium carbonates creates surfaces that deform and flatten under the pressure of the calender nip, helping to maintain sheet gloss and ink holdout. The high gloss and ink holdout obtainable with kaolin clays are difficult to match with both major types of calcium carbonate (GCC, PCC) applications.

Typically, GCC and PCC products have a dry brightness in the range of 95-97%, average particle size of 0.7-2 μm, and specific surface area of 4-12 m^2/g. PCC products typically offer higher opacity benefits since their special morphology design allows for the creation of more internal sheet disruption and air voids, which are responsible for increasing the sheet scattering coefficient.

DISCUSSION:

This paper consists of three parts:

- Theory: Review of aspects of neutral conversions crucial for successful conversion.
- Mill Cases: Examples of mill cases demonstrating how creative applications and understanding of system demands under new conditions benefited papermaking.
- Key Drivers: Analysis of neutral pH conversion and its impact on key mill drivers such as efficiency, brightness, opacity, gloss and printability.

PRINCIPLES OF NEUTRAL pH CHANGE:

pH control:

The significance of change in operational pH reflects the fact that it crosses over the pKa value for the dominant weak acidic group present in the papermaking system – carboxylic function, -COOH. As a result, ionization of the carboxylic group is greatly advanced as reflected in the following changes:

- Increased fiber anionic charge and consequently, improved fibrillation and swelling. This change leads to improved strength development as compared to paper produced at acid pH
- Improved anionic charge measured as total and soluble cationic demand
- Change in the ζ-potential value of the colloidal fraction, including pitch particles. This affects stability and pitch control applications based on fixation.

In the ideal situation, according to Henderson-Hasselbalch's equation (Equation 1), for any weak acid function at pH=pKa the concentration of an acid form (protonated) and a base form are equal.

$$pH = pKa - \log C_{HA} / C_{A} \qquad \text{Equation 1}$$

Increasing pH results in increased anionic charge for carboxylic acids (Equation 2) and decreased cationic charge of protonated amine functions (Equation 3).

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$pK_a \sim 5 \qquad \text{Equation 2}$$

$$R_3NH^+ + H_2O \rightleftharpoons R_3N + H_3O^+$$

$$pKa \sim 8.5 \qquad \text{Equation 3}$$

Both of these equilibria become very relevant at neutral pH papermaking since the higher pH result in both, a buildup of anionic charge of the furnish and a loss of cationic charge of non-quaternary cationic additives. The impact of neighboring acidic or basic functions in polyelectrolytes makes their dissociation curves extend over a wider pH range, but the general conclusions remain unchanged. In the case of polyelectrolytes with on unquarternized amines, protonated ammonium salts functions increase acidity of neighboring groups and further lower the pH level where loss of charge can be observed. Based on results of potentiometric titration of PEI and PVA [7], close to 30% of theoretical cationic charge does not develop even at pH =1. Another important issue beyond the fact of change in the charge value is its variability that affects wet end stability and efficiency. How this charge variation may affect machine stability is well illustrated by Fig.1 that justifies the need for tight pH control.

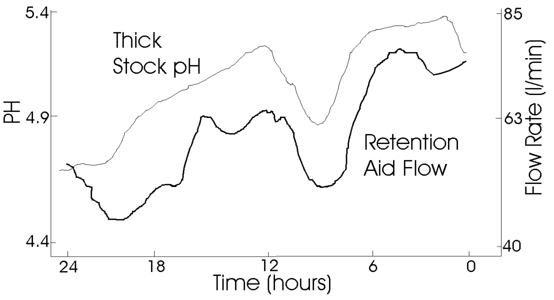

Figure 1: Impact of pH on consumption of a retention aid in the system operating with automatic white water consistency control. This graph illustrates the importance of pH control for systems operating at pH

Introduction of Calcium Carbonate fillers without pH control could result in the papermaking system reaching a pH of 7.8 – 8.2. Since mechanical pulps are highly sensitive to alkaline yellowing processes pH increase has to be controlled so that excessive brightness loss can be prevented. Typical virgin mechanical pulp might lose up to 5 brightness units between pH 6.8 and 8.0 therefore upper limit of pH =7.2 is thus recommended. The sensitivity of deinked furnish is lower and a loss of less than 1 brightness unit may be observed for the same pH change. On the low side, a practical limit of pH=6.8 is accepted and is defined by calcium carbonate solubility. Figure 2 represents the window of pH values for neutral operations with both virgin mechanical and deinked pulps.

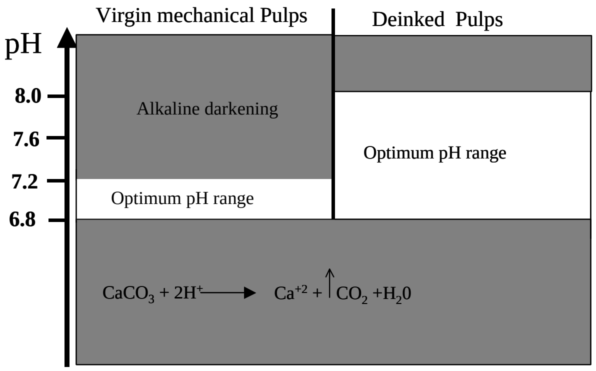

Figure 2: Window of pH available, between calcium carbonate dissolution and alkaline yellowing, for virgin and deinked mechanical pulps.

In some cases, the natural acidity of fresh mechanical pulp is enough to control an equilibrium pH on the machine within an acceptable level, despite the addition of calcium carbonate. In most cases, some form of acid is necessary to prevent brightness increase and consequent brightness losses. Following are some of the most often used pH control strategies:

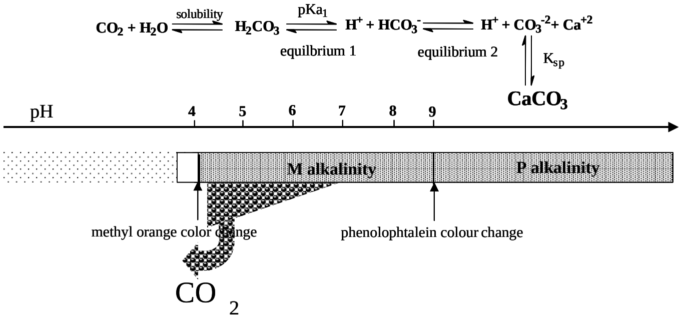

Figure 3: Equilibria involved in CO_2 pH control. At lower pH, around the bicarbonate-carbonic equilibrium the efficiency of pH control becomes less efficient due to CO_2 evolution.

- Sulfuric acid – fundamentally there is no reason why a well-controlled addition of sulfuric acid could not be used., although application of strong acid especially in a open chest leads to higher hardness generation at any given pH level. Use of diluted solution and addition point with good mixing are therefore recommended to avoid local pH drop at addition point.
- Phosphoric acid – less potential for over acidification, safer handling and buffering capacity. Drawbacks - potential for scaling in the areas with pH above 9 (bleaching plant) and increase of phosphates in the mill effluent.
- Carbon dioxide CO_2 – this is a relatively new method used for pH control. Figure 3 represents the basic equilibrium involved in pH control with carbon dioxide. This is an excellent technique for converting P-alkalinity (caustic) to M-alkalinity (bicarbonate) and therefore dropping pH down to the level of pH=8. With pH gradually approaching pH=7 the equilibrium between bicarbonate and carbonic increase CO_2 evolution and significantly reduces the effectiveness of pH reduction. Several mills would utilize trim addition of sulfuric or phosphoric acid to adjust pH at a level close to 7. This may not be required for deinking furnishes with a wider pH operational window. Selection of the proper CO_2 addition point is crucial for successful application. The initial solubility of CO_2 gas can be increased by choosing addition points with lower temperatures and allowing to build certain CO_2 pressure for increased solubility.

- WEC – weak-acid-chelant application [1] combines a weak acid application (phosphoric or CO_2) with sequestering of free metal ions (Ca^{+2} and other). WEC systems offer exceptional brightness results that make them especially suitable for SCA and SCA+ applications.

Retention and Drainage:

Developing filler and fines retention programs is an important part of a neutral conversion project. Authors believe that such retention programs should focus not only on controlling fiber and filler utilization, but also on developing maximum benefits in paper quality – brightness, opacity, strength and gloss. For example, retaining filler particles in the presence of inks in 100% RCF furnish is a case where a high FPAR is not always recommended. Instead, the selectivity of filler retention, managing residence time of fillers and fines within the short loop to reduce their darkening would be more relevant for brightness development in such grades. An entirely different set of expectations and performance criteria may be required for applications where strength, opacity, gloss or print-through are required. Understanding fundamental relationships between sheet structure and paper properties is required to align every application, chemical and mechanical, with developing the sheet properties of interest.

Neutral pH wet end chemistry considerations:

There are several factors that are known to impact the performance of retention and drainage programs. These factors can be divided into two groups – furnish composition and water chemistry. Flocculation, the fundamental process that governs all retention and drainage applications, is strongly affected by adsorption properties and polymer conformation in solution. Surface chemistry, surface charge, surface area, pH, conductivity, cationic demand and hardness are all significantly changed going to neutral pH paper production.

Cationic demand:

As expected, based on the increased degree of ionization of acid functions at higher pH, soluble cationic demand increases with pH. Study performed in preparation for neutral conversion in a hydrogen peroxide bleached SCB mill, indicated about a 30% increase in cationic demand due to a pH increase from pH=5.0 to pH=7.0 (Figure 4). The actual degree of this increase depends on the pulping process involved, with TMP showing higher sensitivity than SGW, PGW and RCF pulps. Hydrogen peroxide bleached pulps show both a higher cationic demand value and a higher change due to pH increase, than pulps bleached under reductive conditions.

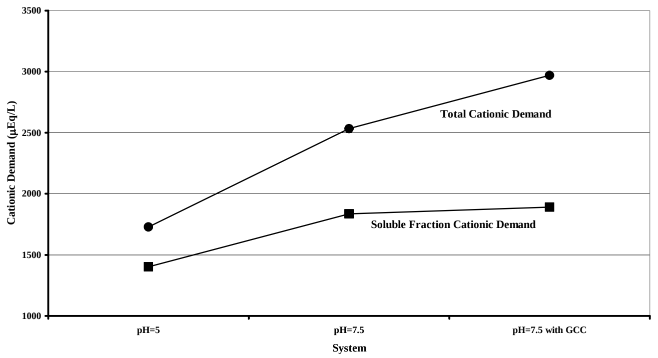

Figure 4: Total and Colloidal/Dissolved fractions of cationic demand for hydrogen peroxide bleached GWD SC furnish at pH=5 and pH=7. Effect of Chalk addition contributes to Total Cationic Demand and significantly less to Dissolve/Colloidal Fraction.

Conductivity:

A moderate increase in conductivity is typically observed going from typical acid to neutral pH applications. For example, in a hydrogen peroxide bleached TMP furnish, conductivity increased by about 10% from 2450 to 2700μS/cm. Although an increase of conductivity typically results in a decrease in drainage, this increase was not large enough to cause drainage issues. Drainage issues could result in reduced couch solids and changes in center roll release, both of which could impact on-machine efficiency. Figure 5 shows the typical variation of drainage properties of TMP newsprint furnish at varying levels of ionic impurities, for a typical dual polymer program. Other types of retention programs showed similar drainage variation patterns [8]. It was also observed that sensitivity of the same retention program to conductivity was slightly lower at pH=7 as compared to pH=5 [8].

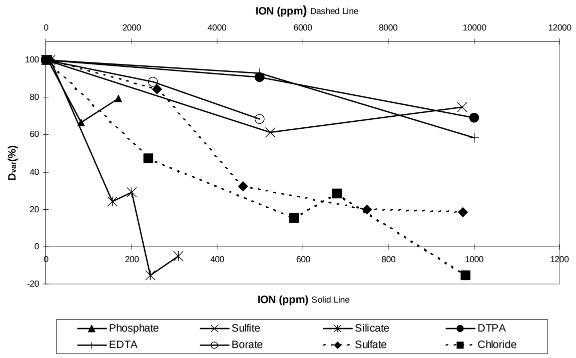

Figure 5: The impact of ionic impurities on drainage variation relative to a "clean" tap water system for a dual polymer program. Other retention programs responded in a similar way. Sensitivity at pH=7 was lower than for an identical system at pH=5.

Fines management:

Since brightness development is one of the underlying reasons for neutral conversions, any potential sources of brightness loss should be investigated, understood and addressed. It is well understood that the solids circulating in the machine short loop darken with time. This applies not only to fillers, which may adsorb some darker substances, but also to fines, which are undergoing a variety of darkening processes. The fines darkening process is somehow unique to neutral pH conversions, since it is practically limited to the combination of higher pH and presence of mechanical pulp fines. Reducing an average residence time of fines in the wet end of the machine through optimization of first pass retention of fines may benefit the papermaker with some recovered brightness, allowing savings in bleaching chemicals costs, improving wet end chemistry in terms of cationic demand and conductivity. Improved wet end chemistry can further improve fines and filler retention leading to a further extension of observed benefits. This is another illustration of the fact that no option for process improvements should be overlooked, as the final impact may far exceed original expectations. Splitting out measurement of retention to fines and fillers retention, when monitoring machine performance, may lead through this optimization process.

Filler retention:

There are a large variety of calcium carbonate fillers available for neutral conversions. Slight cationic ζ-potential value has been claimed for PCC slurries, although in paper machine white water, fast charge reversion takes place due to the adsorption of the negative impurities. Therefore, cationic charge does not survive long enough to benefit the retention process of PCC particles. On the other hand, adsorption of anionic trash, soluble and colloidal by PCC enables some contribution to pitch control.

Calcium carbonate fillers, both PCC and GCC, provide a very economical opportunity for opacity and brightness development.

Figure 6 demonstrates the cost effectiveness of opacity development for various fillers [9]. Calcium carbonates are the most cost-effective of the alternatives for providing both, opacity and brightness.

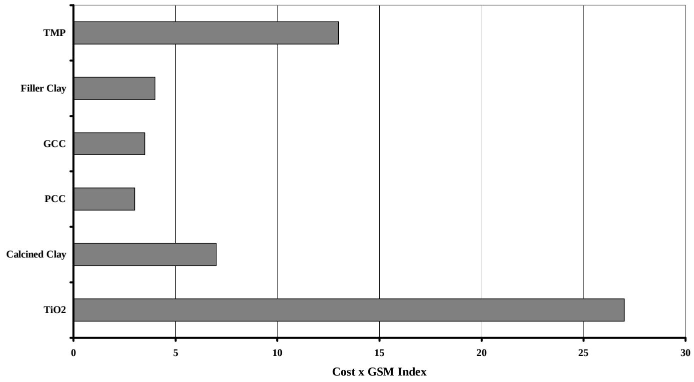

Figure 6: Cost effectiveness of various strategies of opacity development. Cost x GSM index is based on the cost and basis weight of pure component required to reach 90% opacity level.

Saveall operation:

A proper saveall operation is very important for a successful neutral pH conversion. It is necessary to limit the amount of calcium carbonate sent back with cloudy filtrate. If not optimized, understood and corrected, this could lead to changes in pH affecting bleaching operations, generation of excessive hardness levels, calcium oxalate and calcium sulfate scaling and increased machine pitch deposits. Typically, all these problems can be avoided if proactive measures are taken, a good filler retention program is in place and the saveall operates properly. As a general guideline, a FPAR value of 25% or higher is recommended to prevent excessive calcium carbonate filler recirculation throughout the system.

A well-planned neutral pH conversion project must have a chemical scale protection and monitoring program in place. Such a program will always include hardness mapping of the entire mill system. Often, a small addition of machine flocculant to the saveall allows for improved solids recovery and increased drainage without a negative impact on sheet formation. The impact on formation is not limited to aesthetic aspects of non-uniform basis weight distribution. Fundamental sheet properties such as opacity and strength, which may impact On-Machine Efficiency (OME) and the printability of the finished sheet, are also affected.

Pitch and Stickies Control:

Fundamentals of pitch and stickies control remain unchanged as compared to acid applications. Cleaning and screening, while purging detrimental materials as early as possible, remain the most effective and highly recommended strategies. Fixation and detackification are the most widely applied methods to control pitch and stickes remaining in the system despite efforts to eliminate them.

Some important changes resulting from, or coinciding with, neutral pH conversions are:

- With the trend toward high consistency hydrogen peroxide bleaching, many mills have been equipped with highly effective thickening equipment (Twin Wire Presses, Twin Roll Presses) offering the opportunity to remove both soluble and colloidal components of wood pitch. Success with this equipment depends on wood extractives content and the way the mill processes filtrate streams. Often the necessity to recover fiber from this stream by installation of a DAF unit compromises the degree of removal of colloidal extractive materials.
- Higher solubility of acidic fractions of pitch components (resin and fatty acid salts) at higher pH.
- Significantly higher and potentially varying hardness levels creating increased potential of precipitation of calcium salts of fatty and/or resin acids, potential culprits for significant pitch related problems.
- Alum is no longer the principal pitch control agent in the presence of calcium carbonate. Various forms of PAC may to some extent become an alternative as they impact furnish pH to a much lower extent, and are more compatible with calcium

carbonate. Higher charge and lower degree of neutralization PAC products are better in fixation applications and have more impact on pH, but have to be used with more caution.

- Some synthetic fixative materials based on non-quaternary amine function may lose some of their effectiveness through charge loss due to deprotonation at higher pH levels.

Foam control:

Early stages of neutral conversions are typically associated with significant foaming in machine wire pits. This can be associated with an increase in solubility of organic materials accumulated when running at lower pH. A well performing defoamer should be available to counteract this problem. Initial severe foaming subsides with time but a slight increase of defoamer consumption is typically observed in the new conditions.

Linting control:

Surface strength problems normally manifest as linting, dusting, piling and other related issues. These problems are most important for offset printing, especially those with multicolor printing stations sheet fed and web fed. Direct contact with the surface of the blanket, film splitting forces acting in the nip of the press, higher tackiness of the ink, and the accumulation of water in consecutive color stations all put a lot of stress on the surface of the printed paper. It is either the lack of initial surface strength or subsequent loss due to excessive water absorption that are primarily responsible for linting problems. Two widely applied linting treatments to address these two basic linting culprits are as follows:

- Cationic starch application:

better binding fillers and fines in the sheet result in surface strength improvement, requires a special focus at higher pH. Typically, higher cationic demand may require addition of sacrificial coagulant prior to starch addition. This reduces the undesired interaction of starch with anionic trash components and results in improved strength benefits. Increased conductivity has been identified to negatively affect cationic starch retention [10]. An increased degree of substitution of cationic starch typically improves starch retention in such situations.

- ASA sizing:

A sheet produced under alkaline or neutral conditions lacks some of the natural sizing typical for alum treated acid products. This increases water absorption of the sheet produced under neutral pH conditions. Higher pH of operations allows the application of cellulose reactive sizes introduced during alkaline conversions of wood-free grades such as ASA and AKD. Lower water absorption reduces linting propensity for sheets with excessive water absorptivity. In addition, through modification in sheet surface energy, ASA affects the ink transfer process and improves such printing properties as print-through, print density and ink mileage. To avoid deposit issues and improve the efficiency of ASA applications, particularly close attention must be paid to the emulsion quality, good retention, preventing hydrolysis and hardness control. In summary, if the culprit of the linting problem is identified as excessive water absorption, the application of ASA may be an effective solution.

Microbiological Control:

Uncontrolled growth of bacteria and fungi in the papermaking process will negatively impact machine runnability. In acid systems, fungi and bacteria are the predominant causes of microbial deposition, but the growth of bacteria to some extent is hampered by the low pH. As the pH approaches neutral, bacteria, including many species of difficult-to-kill filamentous bacteria, are able to thrive and form thick and often colorful biofilm deposits, particularly if the freshwater treatment is less than adequate [11]. The uncontrolled growth of filamentous bacteria can cause major problems during a neutral/alkaline conversion. When these deposits break loose and fall into the paper furnish or web, they result in end product defects, such as holes and spots or even paper sheet breaks, impacting both machine uptime and saleable product. In addition to deposits, the increased pH allows anaerobic bacteria to thrive [12]. These bacteria form both hydrogen and hydrogen sulfide and are a cause of spoilage in wood fibers in storage towers. A wide variety of antimicrobial agents are employed in order to reduce the colonization of paper machines. Careful selection of the biocides is necessary to determine a program that will be compatible with the bleaching chemistry (reductive/oxidative). Additives should also be treated appropriately to avoid degradation. Appropriate monitoring relies on multiple techniques including plating for aerobes, anaerobes and fungi as needed, microscopy, oxidation reduction potential, pH, ATP, and TRA-CIDE® TOX as appropriate [13]. The level of treatment necessary also depends on the system temperature. If it is high enough, the mill may limit required treatment to fresh water, broke chest and additives.

MILL CASES

Program selection:

Every neutral pH conversion is a significant project for the papermaker, filler company and retention program supplier. Typically a significant retention program evaluation is initiated on synthetic stock prepared to best represent the expected conditions under neutral pH using the calcium carbonate filler planned for the conversion. It has been our observation that a retention program used at acid pH was many times the best, or among the best at the new neutral conditions. Some changes in dosages and feed points, and the development of special applications for improved sheet properties, could evolve later.

pH

Monitoring and control of pH for neutral pH applications should not be limited to the paper machine, but should extend to the entire mill system.

This need of total machine pH control arises from potential losses of brightness in areas where pH exceeds necessary values and excessive hardness development in low pH areas due to Calcium Carbonate recirculation.

Mills producing high brightness products using hydrogen peroxide bleaching for their mechanical or deinked furnishes often use SO_2 to reduce pH after bleaching and remove residual hydrogen peroxide. Dilution of low pH, peroxide bleached TMP, GWD or recycled pulps, may lead to excessive hardness generation with a potential negative impact on pitch control and retention programs. Modification of pH management following peroxide bleaching and targeting higher pH greatly improves this situation. Such a solution may require carry-over of some levels of residual peroxide to the machine, but this does not seem to be a problem in many applications. Several mills greatly benefited from such modifications.

A European newsprint mill using a 100% recycled furnish experienced numerous problems with retention, drainage, brightness and opacity. In order to focus on system stability, Nalco performed standard total mill system audit. When analyzing the mill's data, it became immediately apparent that all problems could be clearly traced to a step change in pH of the system. Figure 7 presents results of the audit in terms of cusum trends for selected values. Further analysis of the system allowed Nalco to trace this problem all the way to final bleaching of recycled fiber done in this mill with hydrogen peroxide. Correction of this issue and introduction of proper pH control on machine resulted in improved wet end stability, retention, filler retention and control over brightness and opacity.

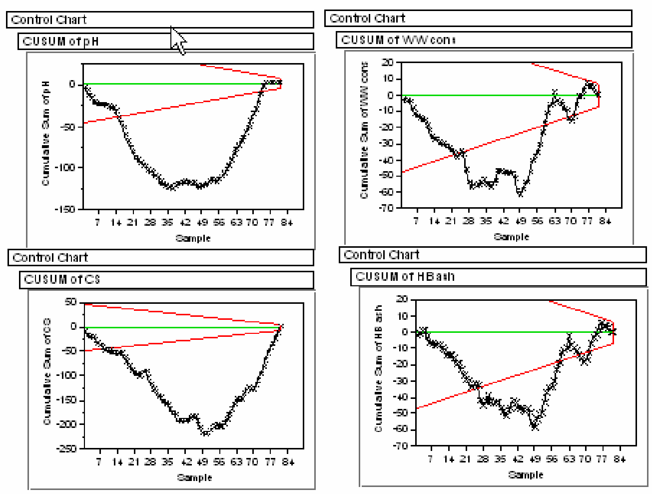

Figure 7: Cusum trends of pH , WW consistency, flocculant addition rate and HB ash all indicate the same general profiles. Problems in the mill could be traced to pH

Improved filler retention:

Success of the neutral pH application requires a well functioning filler retention program. FPAR in the range of 25-35% is adequate even for the highest sheet filler levels. Special application strategies allow to further increase filler retention or drainage without negatively impacting sheet formation. Figure 8 shows the typical results achieved with non-flocculating filler pre-treatment [14]. Pre-treating filler for improved retention will not just increase filler retention but also reduces the cost of the retention program and decouples filler retention from sheet formation. Filler pre-treatment can also be successfully used to boost the brightness benefit from filler retention in 100% RCF furnish by increasing the gap between filler and ink retention. Figure 9 shows the benefit of coagulant/flocculant co-addition that allowed for increased

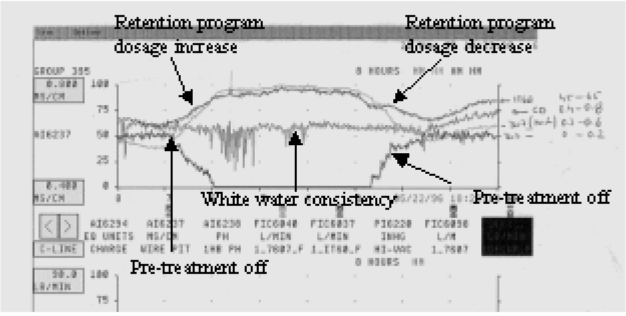

Figure 8: Impact of non-flocculating filler pretreatment on retention additive demand for online consistency control.

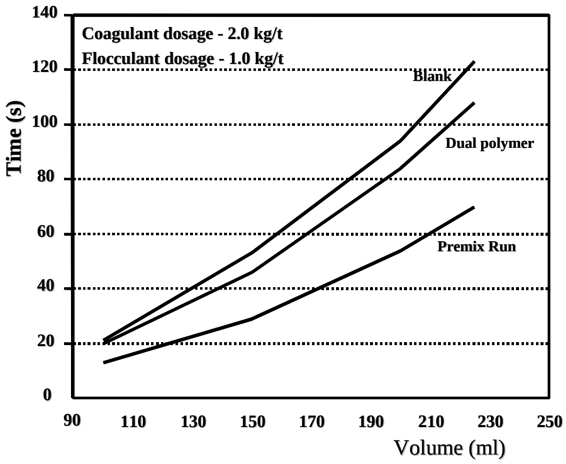

Figure 9: Impact of coagulant/flocculant pre-mixing on the retention program effectiveness in a neutral pH newsprint application.

drainage and filler retention and also resulted in brightness and opacity improvement.

Pitch and stickies control:

Dechandt, Watkins and Pruszynski [15,16] and Richardson[17] described in prior papers a case where corrections to initial neutral pH conversion allowed a mill to regain an initial loss of machine efficiency.

A newsprint mill utilizing mixed TMP and RCF converted to neutral pH and experienced significant difficulties related to pitch issues mainly in the form of calendar stack deposits. The mill converted from acid pH and continued to use a pitch control program based on PEI chemistry. This program was effective at lower pH but showed a significant loss of fixation potential at higher pH. Analysis of deposits collected from the calendar stack showed calcium salts of fatty acids as the main component. On-site testing and elegant analytical work by Richardson [13] confirmed a loss of fixation efficiency of "old" pitch control program to some of the pitch components. The work in the mill was based on filtered turbidity reduction measurements. Richardson [17] applied a gas chromatography technique to analyze components of extractive materials in bound and un-bound fractions. The same work indicated that a novel fixative technology [18]offered superior performance at new pH conditions, and it was selected to treat the TMP pulp stream.

Besides the change of fixation chemistry to better fitting neutral pH conditions, our recommendations at this mill included [15,16]:

- Treatment of both TMP and RCF systems with different fixatives, selected based on filtered turbidity study. Both streams were treated early in the system before blending.
- Introduction of on-line turbidity measurement and development of a control strategy for a fixation program for both streams [15,16,19].
- Additional "polishing" fixative treatment with Hybrid polymer closer to the machine
- Lowering the pH difference between TMP and RCF streams. This was achieved by the CO$_2$ addition to RCF stream.
- A series of mechanical, machine recommendations necessary for utilization of a new retention and fixatives program.

This joint effort with the mill and their corporate R&D group resulted in an 8% increase in OME and numerous sheet quality improvements.

Linting Control:

A newsprint/directory machine using TMP/RCF blend in a 60/40 ratio experienced a severe linting problem. Application of cationic starches previously gave limited improvements. A trial with ASA on this machine showed significant improvement in the number of copies printed between wash-ups from 75,000 to 225,000. This improvement was obtained at a relatively low dosage and cost when compared to cost of other anti-linting technologies. Program performance during the trial was monitored with a water drop test

KEY DRIVERS OF NEUTRAL pH CONVERSIONS

Machine efficiency:

It is well known that the efficiency of the paper machine is significantly impacted by sheet release from the center roll and draws across individual paper machine sections. On a modern machine the sheet release at the center roll represents the first open draw. It is generally understood that a higher pH sheet softer, and more elastic than a sheet produced under acid conditions, especially an alum-treated sheet. This may only partially be related to filler choice with the bulk of this effect coming from higher web pH. It is therefore very important to minimize draws and control release angle from the center roll. The application of a laser device, measuring the distance from the fixed point to the surface of the sheet as it releases from the center roll, allows for on-line monitoring of release properties (Figure 10). This provides an opportunity to make decisions about machine speed changes, center roll release treatment, wet-end additives dosages, etc. Center roll release and draws may also impact a number of sheet properties such as linting, strength, etc. Center roll release properties are impacted by an optimized and stable retention program, drainage, pitch and stickies control, pH and hardness control. Therefore, monitoring the center roll release provides an additional way of monitoring the overall wet end performance.

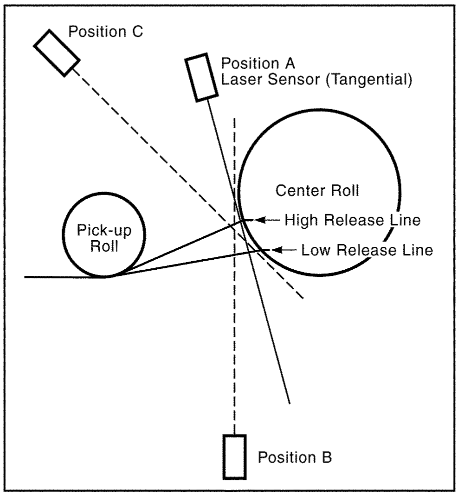

Figure 10: Center roll release position monitoring – an important part of machine efficiency improvement and another window into wet end variability measurement. Optional locations of the laser sensor are shown.

Brightness:

Brightness development becomes the dominant driver in the production of many mechanical grades of paper. Balancing the ability to reach the required brightness level and the costs of brightness development, and minimizing the negative impact of bleaching on machine operations shows the complex nature of brightness management in these grades. Based on the initial brightness level and the required brightness gain, there is a need to develop an optimum brightness development strategy. The most cost-effective strategy may differ for different brightness targets and typically consists of bleaching (reductive, oxidative or combination), filler addition and, at the highest brightness levels, the application of optical brighteners (OBA). Costs of brightness development may reach in excess of $10/1% brightness increase at the highest brightness levels [20]. However, bleaching processes that are not optimized and excessive brightness losses may cost mills millions of dollars in real and "hidden" costs of over-bleaching.

Strutz [6] documented that all types of carbonates, used in 70/30 ratio blend with clays at 32 % filler level, provided a 2-6% brightness increase. GCC and PCC provided a 6% brightness gain while SMC showed significantly less (about 2%). In practical machine applications, the lack of full attention to all areas where brightness is gained or lost may prevent reaching brightness benefits expected from neutral pH conversion and the introduction of new fillers. Operating under higher pH erodes some of the benefit of high brightness fillers usage. Optimization of the retention program and saveall performance is necessary to prevent a negative impact on bleaching operations. Increased selectivity of filler retention in the presence of dark ink particles in 100% recycled furnishes is another area that will increase the brightness benefit. It is clear that the traditional evaluation of a retention program based on its strength as measured by FPR and FPAR may not be what best matches brightness development. Selecting an optimal retention program, application strategy, feed points, control and monitoring strategies should all focus on brightness development.

Opacity:

Although calcium carbonate fillers have refractive indices very close to kaolin fillers, they offer higher opacity benefits despite their high brightness. This opacity benefit does not come at the expense of whiteness through the increased light absorption component of opacity. Within the different types of PCC particles, scalenohedral morphology with its open structure offers higher opacifying effect by increasing internal air voids responsible for light scattering. In the experiments conducted by Strutz [6], blending carbonate fillers at a 70/30 ratio with kaolin clays, at 32% filler level and for 52g/m^2 sheet, an increase of opacity from 1 to 2.5% over clay-only filled sheets, was noted. Again, as in the case of brightness, optimizing chemical retention, avoiding excessive agglomeration of filler and fines, and attempting uniform z-direction filler distribution will additionally boost the opacity benefit of filler application. The preservation of sheet strength is an important side benefit of optimized opacity development with filler retention.

Gloss:

This is a property that is most jeopardized during neutral pH conversion when kaolin clays are substituted by calcium carbonate fillers. Based on experiments by Strutz [6], blending calcium carbonate fillers (70/30 ratio at 32% filler level) resulted in 2-6% Parker gloss loss as compared to clay. SMC performed best and GCC worst with 2% and 6% less gloss as compared with clay filled sheets at the same filler level. Calcium carbonate fillers are in most cases blended with kaolin fillers in SC grade applications for the best combined benefits of brightness, opacity and gloss. GCC, PCC, SMC can be individually combined with clays. Also, combinations of GCC, PCC and SMC can be further blended with kaolin fillers. PCC filled sheets are typically of lower density (higher bulk) improving the efficiency of calendering operations. Additionally, all carbonates, but especially certain PCC morphologies due to their higher microporosity, exhibit higher resistance to calender blackening.

Gloss development in calendering is related to a number of sheet structure properties that can be influenced through the retention program and the mechanical set-up of the forming section. It has been established that air leakage roughness measurements of uncalendered paper shows a poor relationship with final gloss (for PPS r^2=0.40). Other factors such as MFO (Median Facet Orientation) or PV (Surface Pore Volume with 5 μm or 2μm cut-off values) better determine surface features on the length scale relevant to light reflection. These values show an excellent relationship with the gloss (r^2 >0.90) [21]. Scanning Electron Microscopy (SEM), Confocal Laser Scanning Microscopy, Atomic Force Microscopy, Stylus and Laser Profilometry can be utilized to gather surface topography images needed to calculate surface parameters relevant to gloss.

Optimizing filler and fines retention, improving z-direction filler distribution, optimizing drainage profiles, and selection of forming fabrics all can greatly improve surface properties and improve gloss development.

Other properties:

Other important properties resulting from neutral pH conversion that must be accounted for include:

- Increased porosity
- Increased oil absorption– which may lead to excessive print-through
- Increased roughness, especially for GCC, which leads to surface topography changes causing dot reproduction issues and skip dot problem in rotogravure applications
- Changes in tensile strength depend on the type of filler used, with PCC and SMC offering a slight increase and GCC decreasing this parameter.

In practical mill applications, realizing synergies between papermaking practices and chemical approaches may further influence many of the above parameters. Controlling filler agglomeration and filler distribution, improving refining and fiber size distribution, optimizing jet delivery, and modification of the dewatering profile in the forming and press section are only a few of the tools available. Nalco has made a significant effort to understand these relationships and to applying appropriate strategies in the mill environment.

SUMMARY:

Results of neutral pH conversions in mechanical grade production processes depend on the successful, comprehensive management of all aspects of papermaking under dramatically changed process conditions. The potential benefits of such conversions can be easily lost if overall machine management from a mechanical, operational and chemical perspective does not reflect the new reality of working under higher pH conditions and using a chemically reactive filler. A valuable retention and wet-end control program supplier can be a valuable partner in such projects by providing creative deployment of all applications, not just retention programs, providing the opportunity to increase the advantages and reduce the disadvantages of neutral pH conversions in terms of cost, efficiency and quality.

REFERENCES

1. EVANS, B., WRIGHT, R., HASKINS, W.J. and LAAKSO,A.-P., "Filling SC Paper with PCC;A Holistic Approach", PIRA Conference, Miami, 2005.
2. LAUFMANN, M., "Calcium Carbonate Fillers in SC Papers", Woch.Papierfarbikation, 133(11-12), 2005
3. LAUFMANN, M., GISELLA, U., HUMMEL, W., and FORSBLOM, M., "Natural Calcium Carbonate as Filler in Newsprint", Woch. Papierfarbikation, 132(11-12), 2004.
4. GILL, R., "The behavior of on-site synthesized precipitated Calcium Carbonates and other Calcium Carbonate Fillers in Paper Properties", Nordic Pulp and Paper Res. Journal., 2, 120 (1989).
5. GRATTON, R., and PRUSZYNSKI, P., "Potential Incompatibilities in Applications of Chemical Additives", Preprints of Papers, Annual Meeting – Pulp and Paper Technical Association of Canada, 89th. Montreal, 2003.
6. STRUTZ, M.., and BLIXT, T., "Calcium Carbonate Pigments Custom Fit For The Groundwood Market", Preprints of Papers, Annual Meeting - Pulp and Paper Technical Association of Canada, 89th, Montreal, 427-432, (2003).
7. BLOYS van TRESLONG, C.J., and STAVERMAN, A.J., "Poly(ethyleneimine) II. Potentiomatric Titration Behaviour in Comparison With Other Weak Polyelectrolytes", Recueil, Journal of the Royal Netherland Chemical Soc. 93(6), 1974.
8. PRUSZYNSKI, P., JAKUBOWSKI, R., "Impact of Conductivity and Cationic Demand on Drainage of TMP-based Newsprint Furnish", APPITA 56Th Annual Conference Proceedings, 323-331 (2002)
9. IONIDES, G., Temanex Newsletter, 17(2), 8, 2005.
10. BEAUDOIN, R., GRATTON, R. and TURCOTTE, R., "Performance Of Wet-End Starches In Maintaining Good Sizing At High Conductivity Levels In Alkaline Fine Paper," J.Pulp Paper Sci.21(7), J238 (1995).
11. ROBERTSON, L.R., "The Use of Phase-Contrast Microscopy to Assess and Differentiate the Microbial Population of a Paper Mill." TAPPI Journal 76(3) (1993).
12. ROBERTSON, L.R., and SCHWINGEL, W.R., "The Effect of Water Reuse and Conservation on Microbiological Control Programs." TAPPI Papermakers Conference Proceedings. TAPPI PRESS Atlanta (1996)
13. ROBERTSON, L.R. and WALKER, J., "New Monitoring Tools for Microbial Control Programs that Optimize Paper Machine Performance and Minimize Environmental Impact" Presentated at the : 6th New Available Technologies Conference, June 1999, Stockholm.
14. T. TOMNEY, T.,PRUSZYNSKI, P.E, ARMSTRONG, J.R. and R.HURLEY, "Controlling Filler Retention In Mechanical Grades," Pulp and Paper Canada, 99 (8), 66,1998.
15. DECHANDT, A., WATKINS, T, and PRUSZYNSKI, P., "Total approach to deposit control on newsprint machine using TMP and DIP pulp mix - from specialized fixation of individual pulps to retention", APPITA Journal, 57(1), 13-18 (2004).
16. DECHANDT, A., WATKINS, T, and PRUSZYNSKI, P., "Total approach to deposit control on newsprint machine using TMP and DIP pulp mix - from specialized fixation of individual pulps to retention", APPITA 57th Annual Conference Proceedings, 211-218 (2003)
17. RICHARDSON, D., WALLER, N., PARSONS, T., STALLARD, J., YOUNG, M., WATKINS, T., DECHANDT, A." Optimization of neutral papermaking wet end chemistry for pitch free newsprint manufacture", APPITA 57th Annual Conference Proceedings, 219-226 (2003).
18. LaROUX, R., PRUSZYNSKI, P., ARMSTRONG, J,R. LIN, J., POLVERARI M. and ANGELAC, A.P. "Stickies Control in Newsprint Application - Review, Mechanisms and Novel Approach," Pulp and Paper Canada, 98 (9), 54,1997.
19. RENAUD, S., OLSSON, B., and Kamlin, B., New measuring technique enhancing coagulant or fixative control, PIRA Conference, Edinborough, 2000.
20. IONIDES, G., Adding value for improved market competitiveness of mechanical printing papers", Pulp & Paper Canada 105(4), 40-44 (2004*Pulp and Paper Canada 105:4 (2004), 40*)
21. CHINGA, G., "Detailed Characterization of Paper Surface Structure for Gloss Development", Journal of Pulp and Paper Science, 30(8), 222 (2004).

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