THE EFFECT OF MULTI-COMPONENT RETENTION SYSTEMS ON THE PROPERTIES OF THE PAPER SUSPENSIONS

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ABSTRACT

This study presents the influence of retention reagents and multi-component retention systems on properties of pulp suspension which is used during toilet paper production. The following relationships were evaluated: influence of retention systems on rate of pulp suspension water drainage, values of specific cationic and anionic demand, Zeta potential of fibers, WRV values of fibers and water turbidity. The best results were achieved from applying three-component retention system which consisted of micro-milled bentonite Hydrocol OT, modified cationic polyethylenimin Polymín SK and cationic polyacrylamide Percol 830. The above mentioned three-component retention system resulted in increased rate of pulp suspension drainage by 43 %, improvement of water turbidity by 50 % and decrease of specific cationic demand by 33 %. The proposed retention system resulted in improved values of WRV pulp suspensions, which led to decrease of values by about 10 %. Influence of three-component retention system resulted only in minimal decrease of Zeta potential values for fibers.

KEYWORDS: Retention, multi-component retention systems, specific cationic demand, Zeta potential, rate of drainage, WRV, turbidity.

INTRODUCTION

Increase of paper machine speed increases the amount of fibers, especially the fine type, which passes through draining sieves and is lead away with white waters. Loss of fibers, besides economic losses, can present production problems and fluctuation of the produced paper quality. Lost fibers have a great negative influence on water circuits as well as equipment for return obtaining of fibers. One of the ways how fibers can be saved during production of hygienic papers is to enable the best possible retention of fibers on paper machine wires which is possible with the use of retention systems.

Application of a suitable retention system saves fibers but also improves drainage of paper material on the paper machine sieve. This also leads to better drying of paper and it lowers energy consumption of the entire production process.

Benefit in use of retention mechanisms also is very significant from the environmental point of view. Decrease of waste water load with both soluble and insoluble substances, decrease of requirements for processing of sludge and protection of forests based on better use of wood are definite indicators for solving problems associated with saving fibers with modern retention systems.

Retention is one of the major variables of the wet part of the paper machine. It has a significant influence on paper product properties and crossing the paper machine as well as the enviromental impact (Kosonen et al. 2002). Recently incorporating several water circuits and production of papers with lower surface weight required to focus more on the wet part of paper machine.

Conceptually retention is widely understood as percent ratio of solids that are transported to the press part. Currently the most widely used term first-pass retention, which can be calculated in stabilized system based on the solid part consistency and composition of drainage waters.

Retention systems used for improving retention of fine fraction and fillers went through significant changes over the last 40 years. From one-component retention systems used in the 1970s to multi-component retention systems used nowdays.

One-component retention systems used anionic or cationic polymer, which was dosed before or after pressure screen. Such system improves drainage of stock on wire and retain fine fraction and filler. Unfortunately there is a disadvantage of this system in a sence of creation of large floccules which impair paper formation and lower its strength parameters. It does not fix colloid particles, it has lower efficiency in highly loaded systems and it requires high polymer doses.

Two-component retention systems consisting of cationic fixer, cationic starch and cationic or anionic polymer, have the following influence as compared to one-component retention systems: they neutralize anionic charge in the system and fix colloid particles, dyes and wet strength reagents. At the same time, load water is decreased (COD, BOD_5). Formation of large floccules and worse paper formation is a disadvantage of this procedure.

Micro-particle retention systems consist of inorganic micro particles, organic micro polymers and cationic or anionic polymers. Unlike two-component retention systems they exhibit excellent formation on the paper machine wire as well as high efficiency of drainage and neutralization / fixation of bonding impurities and resins. Papers exhibit high strength properties due to excellent formation.

Micro-particle systems enable more efficient draining, retention and formation as compared to traditional retention system. Micro-particle retention systems are used more often for retention of fine fiber fraction and improvement of draining during paper production, especially during production of soft papers. Commercially there are several combinations of micro-particle retention systems available. The main difference between these systems is the type of used micro-particles: anionic silicon oxide, anionic aluminum hydroxide and anionic gel particles of sieved acrylate, bentonite and micro-polymers. (Mizra et al. 2002)

Flocculation with micro-particle systems is different than in two-component polymer systems, however the exact mechanism is not known. It has also been shown that the flocculation degree can be high if micro-particle systems are used. There is an assumption that the difference between micro-flocculation and conventional flocculation is related to the ability of reflocculation of floccules after they are cut. Size of flakes after transformation is small. These microfloccules are evenly distributed throught the entire sheet of paper and therefore distribution of filler as well as the fine fraction is even (Gallagher 1990).

The current micro-particle systems can be separated into several categories depending on the type of micro-particle used, colloid silicon dioxide, bentonite and micropolymer. These systems can be used in various combinations.

Size of primary particles in commercially available colloidal silicon dioxide usually ranges between 1-5 nm. As the base particles are non-porous and approximately spherical, the listed dimensions represent surface area between 500-3000 $m^2.g^{-1}$ (Hubbe 2009).

Microparticles are usually added after a separator where as an aid retention reagent is added before the separator. Microparticles enable a possibility to increase the first breakthrough retention of ash without pre-flocculation. (Gallagher 1990)

In order to improve draining of stock, silicon dioxide is traditionally used in paper industry combined with cationic starch, not with electrolytes.

Bentonite is composed predominately of montmorillonites with traces of silicon dioxide, quartz and other clay materials. The microscopic structure of montmorillonites creates a very high surface area and charge after it becomes dissolved in water. In dry conditions this aluminum-silicate clay is composed of stacked dioctahedral layers about 1 nm thick with a unit formula $Al_2Si_4O_{10}$ $(OH)_2$, in which part of Al ions is substituted with cations of lower valence such as Na, Mg, Li, and so on. This creates unbalance of charge, which is compensated with presence of exchangable cations on the board surface. Theoretical surface area of montmorillonites is about 800 $m^2.g^{-1}$. Cationic exchanged capacity depends on substituting cation but is usually about 1 $meq.g^{-1}$. This leads to very high surface charge about 0.2 $C.m^{-2}$, as compared to cellulose surface charge of about 0.015 $C.m^{-2}$ (Asselman and Garnier 2000).

Degree of swelling depends on salt concentration and the amount of cationic charge. There are two types of bentonite: sodium and calcium. Natural sodium type of bentonite exhibits better swelling properties. Swelling properties of calcium type bentonite are enhanced with sodium hydroxide (synthetic sodium bentonite), i.e., ion exchange of calcium for sodium ions. In dry state, surface area is low (about 12 $m^2.g^{-1}$), but reaches up to 300 - 400 $m^2.g^{-1}$ after swelling in water. Treated form of pure montmorillonite may reach as much as 1000:1. Specific surface area may reach up to 800 $m^2.g^{-1}$, due to its high surface area and high ion exchange capacity. (Norell et al. 1999)

Long chain polymers with high molecular mass (polyacrylamides/ PAM) are efficient during the total retention. In general these low charged polymers are linear, although some branched and structured forms are also used. Linear version is used more often nowdays.

If we want to reach sufficient retention of fine fraction and fillers, PAM's cvrequire generation of large over bridge. In presence of fillers, PAM's may agglomerate particle of fillers which efficiently increases the average value of mineral particles. This increase can jeopardize optical efficiency. Changes in filler distribution in a paper sheet and changes in particle size can be related to deterioration of opacity and formation of sheet, as well as other physical properties. (Polverari and Lewis 2006)

New generation of micropolymers enables flocculation and subsequent formation of sheet structure which maximizes water drainage in the forming zone without pressing. Technology where micropolymers are used is also very effective for retention of calcium carbonate and kaolin. These polymers are synthetized with cationic and anionic charge. (Polverari and Lewis 2006).

Commercal microparticle systems

Nalco Ultra POSITEK (Moore 1999).
CIBA Hydrocol (Ciba 2009).
CIBA Telioform (Harris et al. 2005).

KemForm S - micropolymer (cationic or anionic) + colloid silicon dioxide + flocculant (cationic or anionic PAM or starch)

KemForm B - Micropolymer (cationic or anionic) + bentonite + flocculant (cationic or anionic PAM or starch)

KemForm P - Micropolymer (cationic or anionic) + flocculant (cationic or anionic PAM or starch) + optimal inorganic promoter (PAC / ACH / Alum) (Polverari et al. 2008).

Chemicals Compozil (Moore 1999).

Hydrozil (Moore 1999).

Buckman Mosaic is a retention system which includes 2-4 components. It uses either inorganic microparticles and/or organic cationic micropolymers. Optional third or fourth component can be either PAM and/or cationic polyelectrolyte.

MATERIAL AND METHODS

Material
Pulp types used
Long fiber spruce pulp RMA Botnia
Short fiber birch pulp AKI
Short fiber eucalypt pulp CELTECO
Bleached chemothermomechanical pulp BCTMP METSA

Charge composition of pulps
25 % Long fiber spruce pulp RMA Botnia
32.5 % Short fiber birch pulp AKI
32.5 % Short fiber eucalypt pulp CELTECO
10 % Bleached chemothermomechanical pulp BCTMP METSA

Fibre processing
   The above mentioned pulp charge (450 g b.d. pulp), was milled on laboratory equipment Valley holander, with 2 % consistency, to milling level of 25°SR.

Used chemicals
Percol 830 –cationic polyacrylamide of high molecular weight and high charge (BASF), P830
Hydrocol OT – alkalized micromilled bentonite (Clariant), HOT
Polyflex – three-dimensionally netted polyacrylamide of low molecular weight (BASF), POF
Xelorex – anionic polyacrylamide of low molecular weight and high charge (BASF), XEL
Telioform – anionic micropolymer of very low molecular weight (BASF), TEL
Polymine SK – modified polyethyleneimine (BASF), PSK

Methods
Drainage determination
   For drainage detection Mütek^{TM} DFR-05 detector from BTG Instruments GmbH was used.
   For accurate comparison samples were prepared and tested the same way.

Paper mill sample preparation

The consistency of the fiber suspension should be 0.5 - 2 %. Dilute with sample filtrate if necessary.

Papermaking additive (retention agents) preparation

Prepare a 1 or 0.1 % solution of chemical additive or a concentration applied on site. The desired dosing amount should fit in the 1 - 10 ml pipettes.

Measurement, titration and calculation

First define the stirrer profile according to PM conditions. The following standard values are suggested:

	Duration	Speed
Homogenize pulp	10 s	700 rpm
Chemical contact	10 s	800 rpm (PM speed < 1000 m.min⁻¹)
		1 000 rpm (PM speed > 1000 m.min⁻¹)

Define stop parameters for drainage time or weight; e.g. Stop weight = 800 g, „Stop time" = 60 s.

Enter times for chemical dosages.

Measurement of drainage was performed according to the „Recomended test procedure" in the Operation manual of Mütek^{TM} DFR-05.

A graph of the drainage measurement was generated automatically. The data was transfered automatically to Microsoft®EXCEL.

Particle charge determination

For particle charge detection was used Mütek^{TM} PCD-04 detector from BTG Instruments GmbH. All paper mill samples were prepared the same way.

Paper mill sample preparation

Press Mütek's beaker with 300 μm screen in the fiber stock. Use a syringe and take out at least 20 ml of the supernatant. Put it in a glass beaker and homogenize the sample material.

Papermaking additive (retention agents) preparation

Start with a 0.1 % solution. Depending on titrant consumption increase or decrease additive. Stir the dilution for at least 15 min before titration.

Measurement, titration and calculation

Measurement, titration and calculation of charge demand (solution) or charge quantity (solids) were performed according to the „Recomended test procedure" in the Operation manual of Mütek^{TM} PCD-04.

The formulas for calculating of charge demand (solution) or charge quantity (solids):

$$\text{Charge demand (eq/l)} = \frac{V_{\text{used titrant (l)}} \times C_{\text{titrant (N or eq/l)}}}{V_{\text{sample to be titrated(l)}}} \tag{1}$$

$$\text{Charge quantity (eq/g)} = \frac{V_{\text{used titrant (l)}} \times C_{\text{titrant (N or eq/l)}}}{W_{\text{solids of the sample or its active substance (g)}}} \qquad (2)$$

The system Zeta potential Mütek^{TM} SZP–10

For the detection of Zeta potentials of fibres in aqueous solutions the BTG Instruments GmbH System Zeta Potential Mütek^{TM} SZP-10 we used. The Mütek^{TM} SZP-10 analyses surface charges of fibres and fillers. This is needed to predict the reactivity with additives. Measuring the Zeta potential before and after dosage of an additive will show whether the additive has reacted with the fibre as planned or was misused for the neutralization of the anionic trash. The Zeta potential provides information of the strength of interaction between charged particles. Generally, the stronger the particle interaction, the higher is the Zeta potential. A negative Zeta potential (-mV) indicates that the examined particles/fibres/fillers have a negative overall charge (-); a positive Zeta potential (+mV) indicates particles/ fibres/ fillers with a positive overall charge (+). The Mütek^{TM} SZP-10 uses the streaming potential and other parameters for the calculation of the Zeta potential.

The main part of the Mütek^{TM} SZP-lO is the measuring cell with its two built-in pin electrodes. By applying a vacuum, the sample is sucked into the suction tube and then into the measuring cell. A pulp sample forms a fiber plug on a disposable plastic screen. Thereby, a fibre plug is formed, building up a stationary phase. After a settling time where the fibre plug is stabilized, a set pressure variation of -0.2 bar [-2.9psi] to -0.4 bar [-5.8psi] is applied. An oscillating flow of liquid through the plug is generated. The sheared off counterions induce a streaming potential, which is measured at the electrodes. The measured streaming potential is used to calculate the zeta potential.

WRV determination

Swollen pulp sample was let to drain on the frit SI for 2 - 3 minutes. The brass cups were filled with this pulp to about 2/3 of their height and placed in the centrifuge cells. Next the pulp was let centrifuged for 15 minutes at a speed of 3500 rpm.min^{-1}. Afterwards the samples were carefully removed from the cups and were weighed / m_1 /. Then the samples were dried at 105°C and after drying to constant weight they were weighed again / m_2 /.

Quantity of water and therefore the ability of the pulp to retain water under defined conditions was calculated as follows:

$$\text{WRV} = \frac{m1-m2}{m2} \cdot 100 \qquad (\%) \qquad (3)$$

where: m_1 - weight of the dewatered sample,
m_2 - weight of the dried sample.

Turbidity determination

Turbidity values of water were determined with TURBIDIMETER 2100P from Hach company. In order to determine turbidity, samples were collected from pulp suspension drained water during determination of draining with the use of DFR05 (sieve 60 mesh). Water sample (10 ml volume) was taken after homogenization of the sample and was poured into a cell in order to determine its turbidity value. The measured data is listed in NTU units.

RESULTS AND DISCUSSION

During laboratory tests, we evaluated the influence of various combinations of retention reagents and various retention systems on rate of paper stock draining Zeta potential of fibers, cationic consumption, water turbidity value and WRV fiber value.

Dewatering

Selection of the proper retention reagent or system has a significant influence on rate of draining Fig. 1. Increasing the dose of just single component retention system P830 from 200 to 400 g.t^{-1} led to only slight increase of draining rate, from 460 g at dose rate of 200 to 490 g.t^{-1} dose rate of 400 g.t^{-1} for pulp. For significant improvement of stock draining it was necessary to use multi-component retention systems. Among the two-component retention systems the best draining was achieved for system P830 – 200 + PSK-200 g.t^{-1}, where draining was increased to 602 g and for system   P830-200 g.t^{-1} +HOT-2 kg.t^{-1} draining of 610 g was reached. The highest draining values were obtained for three component retention system P830-150 g.t^{-1} +HOT-2 kg.t^{-1}+PSK-100 g.t^{-1}. Use of this system enabled to increase the draining value to 657 g, which corresponded to 43 % increase as compared to one-component retention system P830-200 g.t^{-1}.
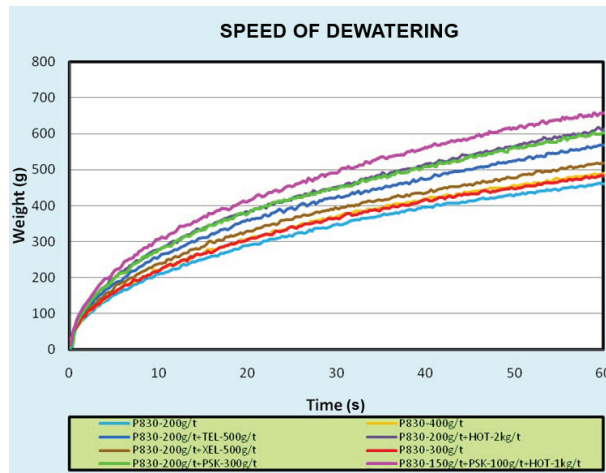

Fig.1: Influence of retention reagents and systems on rate of draining.

Particle charge detection

Fig. 2 illustrates influence of retention agents on specific cationic demand. Based on the obtained data we can assume that one-component retention system RS1, RS2 and RS3 has negligable influence on SCD values. HOT and Polymine SK of systems RS4, RS7 and RS8 have the greatest influence on SCD values. Applying two-component retention system RS4 results in decrease of SCD values by 24 ueq.l^{-1}, in case of RS8 system by 33 ueq.l^{-1} and in case of RS7 system by 37 ueq.l^{-1}.

Detection of WRV

Influence of retention reagents and systems on WRV fiber suspension values is shown in Fig. 3. From all retention systems the two-component retention systems RS4, RS7 and three-component retention system RS8 have the greatest influence on WRV values. RS4 and RS7

retention systems resulted in decrease of WRV values by 6-7 % while the RS8 system resulted in retention increase by as much as 10 %.
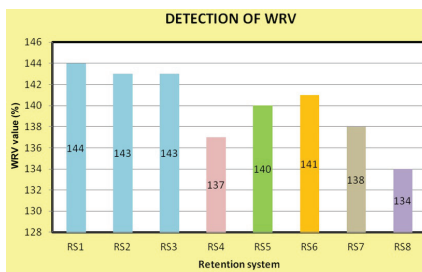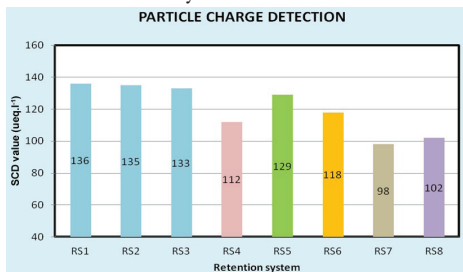

Fig. 2: Influence of retention reagents and systems on specific cationic demand value.

Fig. 3: Influence of retention reagents and systems on WRV values of stock.

Turbidity detection

As shown in Fig. 4, suitably selected retention reagents and systems significantly influence water turbidity. Applying retention systems RS4 and RS5 significantly reduced turbidity where turbidity values decreased by 43-48 %, from original 165 NTU to as low as 86 NTU. The best results related to decrease of turbidity values were obtained in case of three-component retention system RS8. Turbidity values decreased from 165 NTU to 82 NTU, which corresponds to decrease by 50 %.
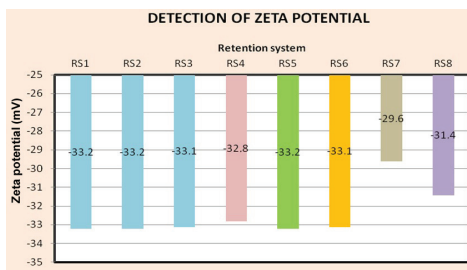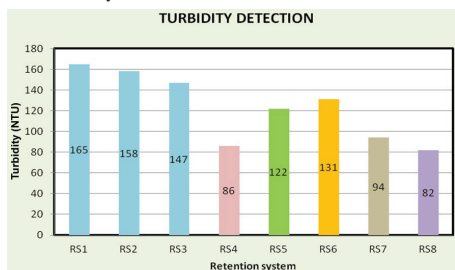

Fig. 4: Influence of retention reagents and systems on water turbidity values.

Fig. 5: Influence of retention systems on Zeta potential of fibers.

Detection of Zeta potential

The greatest influence on Zeta potential change of fibers corresponds to retention systems RS7 and RS8. These systems include a highly cationic polymer Polymine SK (Fig. 5). Depending on its dose in retention system at dose rate of 100 g.t^{-1} in case of system RS8 Zeta potential would decrease from the original -33.2 to -31.4 mV and at dose rate of 200 g.t^{-1} v RS7 system, Zeta potential would decrease to -29.6 mV.

Dewatering vs turbidity

Comparison of influence of various retention systems on rate of pulp suspension draining and turbidity of drained water shows that there is dependence between rate of draining and turbidity (Fig. 6). When an individual retention system was more efficient in water turbidity decrease, rate of pulp suspension draining increased. The best quality of water based on turbidity as well as the higher rate of draining was obtained in case of the three-component retention system RS8.
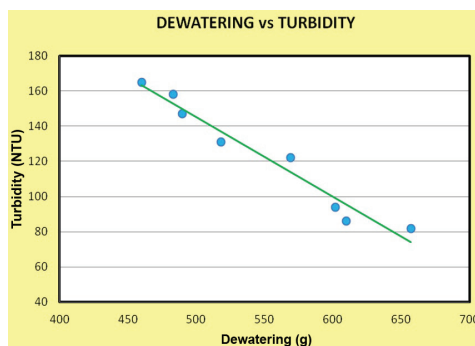
Fig. 6: Dependence between the pulp suspension draining rate and turbidity of drained water.

CONCLUSIONS

The suitable retention reagents or systems significantly influence the properties of stock. Influence of retention reagents and systems had the greatest influence on rate of pulp suspension draining, turbidity values and specific cationic demand values. System RS4 P830-200 $g.t^{-1}$ +HOT-2 $kg.t^{-1}$ turned out to be the most effective. Applying this retention system resulted in increase of draining by 33 %, decrease of specific cationic demand by 18 % and enhancement of turbidity values by about 48 %. This two-component retention system enabled to decrease WRV values of stock by 7 %. Its influence on Zeta potential of fibers is practicaly negligable.

The best results were obtained when triple retention system P830-150 $g.t^{-1}$+HOT-2 $kg.t^{-1}$ +PSK-150 $g.t^{-1}$ was applied. The rate of pulp suspension draining increased by 43 %, water turbidity improved by 50 % and WRV values improved by 10 %. Specific cationic demand of water decreased by 34 $\mu eq.l^{-1}$, which represents a drop of 33 %. Influence of three-component retention system on Zeta potential was negligable. The original value -33.2 decreased to -31.4 mV.

Application of the suitable retention system results in improvement of stock and water properties which enables to assume that there is eventually better draining on the paper machine wire, obtaining higher dry matter in press and decrease of steam consumption in the drying area of paper machine. At the same time conditions are created which increase performance and runnability of the paper machine.

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