

# LICENTIATE THESIS

## AKD Sizing - Dispersion Colloidal Stability, Spreading and Sizing with Pre-flocculated Dispersion

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**Licentiate thesis**

Institutionen för Kemi och metallurgi  
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# **AKD sizing – Dispersion Colloidal Stability, Spreading and Sizing with Pre-flocculated Dispersions**

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**February 2002**

## Abstract

Alkylketene dimer, AKD, dispersions are used in the paper industry to obtain paper grades with a hydrophobic character i.e. resistance to sorption of water. AKD is used in neutral to alkaline internal sizing, pH in the interval of 6–9. AKD dispersions consist of wax particles emulsified in water. The particles are electrostatically and in most cases also sterically stabilized by cationic polyelectrolytes. The size of the particles is usually in the range of 0.5–2  $\mu\text{m}$  in diameter. The idea of having cationic particles is that they are supposed to be deposited onto the negatively charged fiber surfaces, heterocoagulation. An increased usage of recycled pulp and a closure of the wet-end circuits of the paper machine will lead to increasing levels of dissolved and colloidal substances. These substances could be detrimental by affecting the AKD deposition onto the fiber material and the colloidal stability i.e. induce flocculation of sizing particles. Flocculation could lead to an inhomogeneous distribution of the sizing agent. The aims addressed in this thesis were the following:

- to investigate if high levels of shear, electrolyte concentration, anionic polymers and surfactants could affect the colloidal stability and induce flocculation of differently designed AKD dispersions
- to study the migration of AKD and the influence of extractives on the migration
- to study the sizing efficiency and retention using flocculated dispersions

The colloidal stability of the dispersions was tested under shear by measuring the particle size distribution and the microelectrophoretic mobility. The migration of AKD through paper sheets with defined thickness and through paper sheets impregnated with extractives was analyzed with contact angle measurements on stored samples. The sizing efficiency of flocculated AKD was determined by measuring 60-second Cobb and contact angles on laboratory sheets. The retention of AKD was determined by quantitative analysis of the AKD content in the laboratory sheets using alkaline hydrolysis followed by solvent extraction and quantification with capillary gas chromatography.

It was shown that anionic polymers and surfactants could seriously affect the colloidal stability of the dispersions, while shear and electrolyte concentration had a small influence. Dispersions with a high surface charge flocculates easier than dispersions with a low surface charge in process water from the wet-end of a linerboard paper machine. The flocculation rate is fast and occurs on the same time scale as deposition onto fines and fibers. The AKD agglomerates could be up to 30  $\mu\text{m}$  in diameter even at high levels of shear.

The AKD diffusion coefficient in paper sheets was estimated to be  $10^{-11} \text{ m}^2/\text{s}$  at a temperature above the melting point of the wax. The results indicate that extractives

do not interfere with the AKD migration. A reasonable explanation is that migration occurs via the vapor phase.

It was also shown that sizing with flocculated AKD improved the sizing efficiency significantly due to increased retention. This clearly indicates that migration is efficient and that agglomerates can be used for internal sizing provided that the flocculation process is controlled. The conventional picture that the sizing agents must be very evenly distributed to achieve efficient sizing could, from the viewpoint of these results, be questioned.

The process of sizing with pre-flocculated AKD dispersions is the subject of a patent application.

Even if this thesis is focused on AKD dispersions, the obtained knowledge should be possible to transfer to other sizing systems. The emulsification process for rosin and ASA is based on the same principles as for AKD.

## List of papers

This licentiate thesis is based on following papers, herein referred to by the their Roman numerals:

**I. Colloidal stability of alkylketene dimer (AKD) dispersions. Influence of shear, electrolyte concentration, polyelectrolytes and surfactants**

**Rosa Mattsson, Johan Sterte and Lars Ödberg.**

The Science of Papermaking, edited by C.F Baker. 12<sup>th</sup> Fundamental Research Symposium Vol. 1:393-415, Oxford, UK, 2001.

**II. Influence of abietic acid, betulinol, sodium oleate and tripalmitine on the migration of alkylketene dimer (AKD) in paper**

**Rosa Mattsson, Dan Lindström, Johan Sterte and Lars Ödberg.**

Manuscript

**III. Sizing with Pre-flocculated Alkylketene Dimer (AKD) Dispersions**

**Rosa Mattsson, Johan Sterte and Lars Ödberg.**

Submitted to Nordic Pulp and Paper Research Journal

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# 1. Introduction

Internal sizing is a widely used process in the paper industry to produce paper grades with hydrophobic character, such as liquid board, linerboard and printing papers. Paper grades with a hydrophobic character have a good resistance to sorption of water. The hydrophobicity of a paper is also important to control the printability. Internal sizing is conventionally divided in two areas, depending on the pH of the fiber stock, acid sizing and neutral sizing. In the acid sizing, a combination of rosin and alum is used. Neutral sizing is usually achieved either with alkylketene dimer, AKD, or alkenyl succinic anhydride, ASA. AKD and ASA have become more frequently used in the industry during the last decade, not least for economical reasons. Internal sizing at neutral pH gives the possibility to use calcium carbonate as a filler. Another benefit that neutral sizing gives is that the paper gains an improved storage durability compared to rosin sized paper e.g. archive papers. For a comprehensive overview on sizing, Roberts [1] is recommended.

The neutral sizing agents are most commonly introduced into the paper machine as dispersions. In the dispersions the sizing agent exists as small spheres with an average diameter of 0.5–2  $\mu\text{m}$ . The spheres are electrostatically and in most cases also sterically stabilized with polyelectrolytes. The purpose of manufacturing the sizing agents as dispersions is that they are easy to handle in the mill. Dispersions of rosin size and AKD can be stored for months, whereas ASA has to be dispersed at the mill due to hydrolysis of ASA. The dispersions can be diluted with water, which facilitates the dosage strategies.

The work presented in this thesis is based on AKD, therefore the rest of the introduction will focus on AKD. AKD sizing is well described in the literature [2 - 5] and the general opinion is that the internal sizing can be described as follows:

- retention where the cationic charged AKD particles are deposited onto the negatively charged fiber surface via heterocoagulation
- a homogeneous distribution of the micron-sized AKD particles on the fiber surface is desirable
- spreading of the AKD wax on the fiber surface in the dryer of the paper machine
- anchoring of the AKD to the cellulose via a  $\beta$ -ketoester bonding

AKD dispersions are commercially available with a solids content of 10–30 %, where about 80 % of the solids content consists of AKD. A normal addition of AKD is around 0.1–0.2 % solids content based on dry pulp. The retention (AKD found in the produced paper divided by the added amount) is generally low and lies around 30–50 %. However, new analytical methods have been developed that are

able to determine the content of polymerized AKD [6], which probably will reevaluate the general figures of AKD retention.

Increasing levels of dissolved and colloidal substances in the wet-end of a paper machine could affect the retention of the sizing agent. Substances originating from the wood like electrolytes, hemicellulose, lignin and extractives are referred to as dissolved and colloidal substances. These substances can, at high levels, reverse the charge of the AKD particles and prevent attachment to the fibers. The suppliers manufacture the AKD dispersions to suit different paper grades, different wet-end systems and increasing paper machine speeds [7–8]. For instance, to improve the retention of AKD in wet-end systems having high levels of dissolved and colloidal substances dispersions with a high surface charge are recommended to avoid problems with low retention.

A low retention will lead to increasing levels of AKD that circulates in the wet-end system, which could induce agglomeration of the sizing particles.

Agglomeration of the sizing agent could lead to a poorer distribution and problems with scaling and spots in the produced paper. On the other hand if AKD spreads efficiently an inhomogeneous distribution would not be a problem. Larger AKD particles or agglomerates of AKD would then be preferable to use, since large particles are easier to retain in the sheet.

In the literature there are different proposals for the spreading mechanism of AKD. Some authors have suggested that AKD completely wets the cellulose surface and spreads to a mono- or to a thin multimolecular layer, and that the spreading rate increases with an increasing temperature [9–10]. Garnier et al. [11–12] investigated the spreading of pure AKD wax and a commercial AKD dispersion on smooth model surfaces of glass and cellulose, and they could not observe a complete spreading of the wax nor of the commercial dispersion. Seppänen et al. [13] proposed that the spreading mechanism is a surface diffusion with an autophobic monolayer precursor. Shen et al. [14] suggested that AKD over its melting point most likely spreads via the vapor phase.

High levels of extractives could be detrimental to the AKD spreading process. Lindström et al. [15] have reported that sodium oleate on the fiber surfaces prevent AKD to spread and to be anchored to the cellulose.

## **2. Objectives**

The aims of this work were:

- to investigate the colloidal stability of AKD dispersions with different compositions exposed to high levels of shear, electrolyte concentration, anionic polymers and surfactants
- to investigate the influence of extractives on the migration of AKD in laboratory sheets
- to study the sizing efficiency and retention using flocculated AKD dispersions

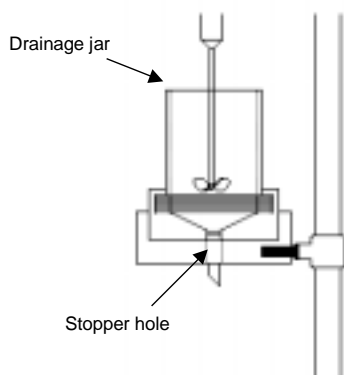
## 3. Experimental

### 3.1 Experimental techniques and methods

The experimental techniques and methods are briefly described in this part, more comprehensive and detailed descriptions are given in Papers I-III.

#### 3.1.1 Britt Dynamic Drainage Jar

The Britt Dynamic Drainage Jar, BDDJ, [16] supplied from Paper Research Materials Inc., USA, is a laboratory device for conducting retention experiments under controlled conditions e.g. standardized levels of shear. The BDDJ is shown in figure 1.



**Figure 1.** Schematic picture of the Britt Dynamic Drainage Jar.

The sample is placed in the jar and the selected shear is produced by adjusting the stirring speed of the propeller. A mesh or a screen-plate is dividing the cylindrical from the conical part of the BDDJ. In standardized methods a screening device of 200 mesh is recommended. The sample is collected by opening the drain cock placed in the stopper hole.

The BDDJ was used in the experimental setup for studying the colloidal stability of the AKD dispersions and used for pre-flocculation. The AKD dispersions were added to synthetic and real white water samples in the jar and stirred at speeds ranging from 1000–2000 rpm. The samples were immediately analyzed with respect to particle size distribution and z-potential. The first 100 ml of the sample was discarded.

### **3.1.2 Particle size distribution**

The particle size distribution was measured using laser diffraction [17]. The particle size distribution measurements were made with a Malvern Mastersizer Microplus, Malvern Instruments Ltd., UK. The size range of the instrument is 0.05 - 556  $\mu\text{m}$ . The data was analyzed according to a polydispersive model, 5OHD, supplied with the instrument. This model uses the Mie theory. A particle refractive index of 1.15, an imaginary refractive index of 0.1 and a refractive index for the medium (water) of 1.33 were used.

### **3.1.3 Microelectrophoretic mobility (z-potential)**

The z-potential of the AKD particles was determined by measuring the microelectrophoretic mobilities [18]. The z-potential was measured with a ZetaSizer 2000, Malvern Instruments Ltd., UK.

### **3.1.4 Polyelectrolyte titration**

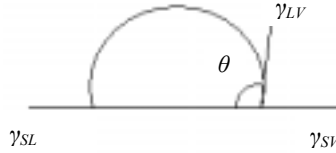
The polyelectrolyte titrations were performed in two different detection modes, streaming current [19] and photometric detection using o-toluidine blue, OTB, [20]. The function of the streaming current detector is to create a high flow rate in the sample in order to separate the counterions from the polyelectrolytes attached to the piston or the walls of the sample vessel. A piston closely fit to the narrow cylindrical section in the sample vessel creates a high flow in the sample. The streaming current is created when the counterions are separated from the polymers. The sample vessel contains two electrodes that collect the streaming current and convert it to the corresponding potential. A polyelectrolyte with opposite charge is added in portions to the sample until the potential reaches zero (end point of the titration). The polyelectrolyte titrations with streaming current detection were made with a Müttek PCD 03 pH, Müttek Analytical, Germany.

Using photometric detection, the samples with known additions of OTB, and polydiallyldimethylammonium chloride, poly-DADMAC were titrated with potassium polyvinylsulphate, KPVS. At the point where all the poly-DADMAC has reacted with either the anionic components in the sample or the added KPVS, further additions of KPVS complexes with OTB converting its color from blue to pink. The absorbency was measured at 515 nm and 650 nm using a Phototitrator 94, BASF, Germany.

The charge density of the AKD dispersions was analyzed using streaming current detection and the cationic demand of the white water samples was analyzed using photometric detection.

### 3.1.5 Contact angle

One way to investigate the hydrophobicity of a paper surface is to measure the contact angle,  $\theta$ , with water. If a drop of water is placed on a smooth surface, it will under certain circumstances form an angle with the surface as seen in figure 2.



**Figure 2.** A liquid drop placed on a smooth surface gives an equilibrium angle,  $\theta$ , depending on the surface tension of: the interface between the surface and the vapour phase,  $\gamma_{SV}$ , the interface between the surface and the liquid,  $\gamma_{SL}$ , and the interface between the water and the vapour phase  $\gamma_{LV}$ .

At equilibrium the contact angle,  $\theta$ , is related to the three surface tensions according to Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (1)$$

Young's equation is only valid for planar surfaces, but is used for papers with a correction for the surface roughness [21]. A contact angle  $\geq 90^\circ$  implies non-wetting conditions i.e. water penetration into the fiber structure does not occur. Water completely wets the paper surface if the contact angle is  $0^\circ$ , and partly wets the surface if the contact angle at equilibrium is between  $0^\circ$  and  $90^\circ$ . Diffusion of water vapor might still occur, since this diffusion does not depend on surface tension. A paper is considered to be sized when the contact angle of water at equilibrium is  $\geq 90^\circ$ .

The contact angle measurements were made with micron-sized drops of distilled water with a volume of  $4.0 \mu\text{l}$ . The contact angles were measured 0.1 seconds after the drops were applied to the paper surface. The reported contact angle is the average of ten individual measurements.

The contact angle measurements were made with a Fibro1100DAT (FIBRO Systems AB, Sweden).

### 3.1.6 Surface energy

To determine the total surface energy of the paper samples contact angle measurements and an extended form of Young's equation were used [22]. The total surface energy is given by:

$$\gamma_{tot} = \gamma^{LW}_{Solid} + 2(\gamma^+_{Solid} \cdot \gamma^-_{Solid})^{1/2} \quad (2)$$

where  $\gamma_{\text{tot}}$  is the total surface energy,  $\gamma_{\text{Solid}}^{\text{LW}}$  is the dispersive (Lifshitz-van der Waals) component,  $\gamma_{\text{Solid}}^+$  is the Lewis acid component and  $\gamma_{\text{Solid}}^-$  is the Lewis base component of the paper surface energy. Only the total surface energy is reported here.

The contact angle measurements were performed with three different liquids with known surface tension properties; diiodomethan which is a non-polar liquid and only has a dispersive,  $\gamma^{\text{LW}}$ , contribution to the surface tension and two polar liquids distilled water and formamide which besides dispersive have Lewis acid,  $\gamma^+$  and Lewis base,  $\gamma^-$ , contributions to the surface tension. The surface tension properties of the liquids are given in [23].

The contact angles used in the calculations were the average of 10 individual measurements. The contact angle was measured 0.1 seconds after the drop was applied to the paper surface. The volumes of the drops in the measurements were 2.1  $\mu\text{l}$  for diiodomethan and 4.0  $\mu\text{l}$  for distilled water and formamide.

The contact angle measurements were performed with a Fibro1100DAT, (FIBRO Systems AB, Sweden).

### 3.1.7 Dynamic sheet former

A dynamic sheet former, Formette Dynamique, Centre Technique du Papier, France, was used for producing the laboratory sheets. The sheets are formed on a mesh placed on a rotating drum. The fiber stock is dispersed and applied onto the mesh under pressure through a nozzle. The drum speed and the fiber stock speed is set individually to produce papers with requested fiber anisotropy i.e. fiber orientation in the sheet.

### 3.1.8 60-second Cobb

60-second Cobb was used to measure the water sorption into the laboratory sheets. The 60-second Cobb ( $\text{g}/\text{m}^2$ ) gives the absorbed amount of water on an area of 1  $\text{dm}^2$  when one side of the paper sheet is exposed to a water pressure of 1 cm for 60 seconds. The 60-second Cobb is calculated according to:

$$60\text{-second Cobb} = 100(a-b) \quad (3)$$

where  $a$  is the weight of the sheet exposed to water and  $b$  is the weight of the sheet before exposure. Special apparatus are designed for Cobb measurements, and examples of those are described in the standard method for Cobb measurements, ISO 535:1991.

## 3.2. Materials and experimental procedures

### 3.2.1 Characteristics of AKD dispersions

Three dispersions with different compositions were chosen to cover product groups on the market. The dispersions were made from the same AKD wax, with a melting point of 52–53 °C and the average size of the AKD particles was approximately the same, 0.5–0.8 µm in diameter. The only difference between the dispersions was the surface charge, attained by using different stabilizing polymers.

Dispersions A and B with PA were stabilized with cationic starch, which also provides them with steric stabilization. Dispersion A had the lowest charge density. B with PA had a medium charge density and also contained a polyaluminum salt (PA). Dispersion C had the highest charge density and was stabilized with cationic polyamideamine. Dispersion C should be less sterically stabilized than the other two. The charge densities were measured with polyelectrolyte titration with streaming current detection. The microelectrophoretic mobility (z-potentials) of the AKD particles was also measured.

The stabilizing polymer, the solids content and the AKD content of the dispersions are presented in table 1.

**Table 1.** Properties of the AKD dispersions.

Dispersion	Stabilizing polymer	Charge density of polymer	Solids content % w/w	AKD content % w/w
A	Cationic starch	Low	10	7.7
B with PA In Paper III B(PA)	Cationic starch (polyaluminum salt)	Medium	13.3	10
C	polyamideamine	High	10	8.9

The charge density and the z-potential of the dispersions at two different pH levels are given in table 2. The charge density of B with PA was lower at pH 7 than at pH 3–4 (pH in the received products), most probably due to conversion of positively charged aluminum complexes to aluminum hydroxide. The charge density of dispersion A could not be determined with accuracy. The titration curves showed no distinct end point. The result for A presented in table 2 only gives an estimate.

**Table 2.** The measured charge densities and z-potentials of the AKD dispersions. The figures in the table are the average value with 95 % confidence intervals.

Dispersion	Polyelectrolyte titration as received $\mu\text{eq/g}$	z-potential as received mV	Polyelectrolyte titration pH 7 $\mu\text{eq/g}$	z-potential pH 7 mV
A	16	$12 \pm 0.7$	26	$3.6 \pm 0.5$
B with PA In Paper III B(PA)	$270 \pm 10$	$20 \pm 0.7$	$120 \pm 3$	$14 \pm 1$
C	$640 \pm 6$	$67 \pm 2$	$580 \pm 20$	$33 \pm 1$

Eka Chemicals Ltd., UK prepared the dispersions. They were stored at  $4.0 \pm 2.0$  °C and were used within 3 months after preparation.

The dispersions were used in Paper I and Paper III. The dispersion concentration is given as solids content. The AKD dosage in Paper III refers to the solids content of the AKD wax in the dispersion.

### 3.2.2 Colloidal stability of AKD dispersions

The colloidal stability of the AKD dispersions was studied under shear in a Britt Dynamic Drainage Jar by measuring the particle size distributions and the microphoretic mobilities.

The influence of shear, electrolyte concentration, polyelectrolytes and surfactants was investigated. The stability tests were made at a dispersion concentration of 75 mg/l and a pH of 7 (phosphate buffer) unless otherwise stated.

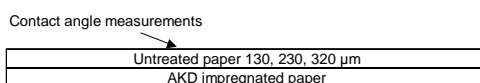
### 3.2.3 Migration of AKD

The migration of AKD through paper sheets of different thickness and also through paper sheets impregnated with extractives was studied by measuring the obtained contact angle with water as a function of storage time. The paper sheets were made from Elementary Chlorine Free, ECF, bleached softwood pulp with an extractive content less than 0.1 % w/w in the dynamic sheet former at three grammages. The sheets were pressed two times at 6 bar in a felted laboratory press and dried at 80 °C in a STFI Sheet Dryer, Fibertech AB, Sweden. The AKD wax used in the study was based on hardened tallow fatty acids and had a melting point of 52–53 °C. Impregnation was made by immersing the sheets in solvent solutions of abietic acid, betulinol and tripalmitine. Sheets containing sodium oleate were made with the dynamic sheet former, where sodium oleate was added into the fiber stock. The samples were stored for different times at two different temperatures, 80 °C and 105 °C. The total surface energy of the sheets were determined by contact angle measurements. Solvent extraction and quantification with capillary gas

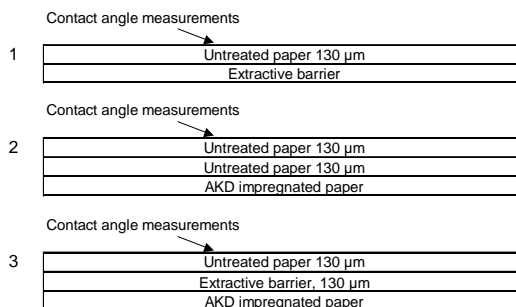
chromatography were used to determine the content of the impregnating agents in the sheets.

The samples were prepared by placing paper strips in layers according to figures 3 and 4. The samples were wrapped in aluminum foil and stored in a heating cabinet under a weight until contact angles with water were measured. A separate sample was made for each storage time. The contact angles were measured on the top of the untreated paper i.e. the surface not being in contact with the AKD or extractive impregnated papers.

Migration time through the sheet was defined as the time to reach a contact angle of 90 °.



**Figure 3.** Samples for studying the AKD migration through sheets with different thickness. The samples were prepared by mounting untreated paper strips with different thickness on AKD impregnated paper strips. The contact angles with water were measured on the side of the untreated paper not being in contact with the AKD impregnated paper. The samples were stored for different times at 80 °C and 105 °C before the contact angle measurements.



**Figure 4.** Samples for studying the AKD migration through papers impregnated with extractives. The samples were made as follow: **(1)** one untreated paper strip on top of a paper strip impregnated with extractive for studying the diffusion of the extractives themselves through paper. **(2)** two untreated paper strips on top of an AKD impregnated, reference samples. **(3)** one impregnated paper strip in the middle of an untreated and an AKD impregnated strip for studying the AKD migration through a paper impregnated with extractive. The samples were stored for different times at 80 °C before the contact angle measurements.

### **3.2.4 Pre-flocculation and internal sizing with AKD agglomerates**

AKD agglomerates were used for sizing laboratory sheets. The pre-flocculation step was performed by flocculating dispersion C with carboxymethylcellulose, CMC, or white water, and then the flocculated dispersion was added into the fiber stock. The flocculation was achieved by adding the amount of CMC or white water bringing the system to a z-potential close to zero.

The laboratory sheets were made from Totally Chlorine Free, TCF, bleached hardwood in a dynamic sheet former. The sheets were pressed twice in a felted laboratory press at 6 bar and dried at 80 °C for 11 minutes in a STFI Sheet Dryer. The laboratory sheets were stored overnight in a conditioning room before the 60-second Cobb measurements. The sheets were not cured at higher temperatures before the Cobb measurements.

Contact angle measurements with water and the total amount of AKD in the sheets were analyzed three weeks after the sheets were made. The amount of AKD was determined by alkaline hydrolysis followed by solvent extraction and quantification with capillary gas chromatography [24].

## **4. Results and discussion**

### **4.1 Colloidal stability of AKD dispersions**

Ongoing trends in the paper industry are to minimize the fresh water consumption and to increase the usage of recycled fibers. This can lead to increasing levels of dissolved and colloidal substances in the white water systems. These substances could impair the AKD retention, which consequently can lead to a higher amount of AKD circulating in the wet-end system. A higher degree of non-retained AKD could cause problems with agglomeration. Agglomeration could possibly impair the sizing efficiency, since agglomerates would probably be unevenly distributed onto the fiber material. AKD agglomerates could also cause problems with scaling and spots in the paper.

Higher production speeds are constantly requested which will require dispersions that are able to tolerate high turbulence levels.

The objective of the work reported in the first paper was to investigate how cationic AKD dispersions, commercially available today, tolerate high levels of shear, electrolyte concentration, anionic polymers and surfactants. The colloidal stability of differently designed AKD dispersions (described in table 1) was tested without fibers present. The kinetics of AKD flocculation was studied experimentally in order to answer if flocculation is a process to consider during papermaking.

### 4.1.1 Influence of shear and electrolyte concentration

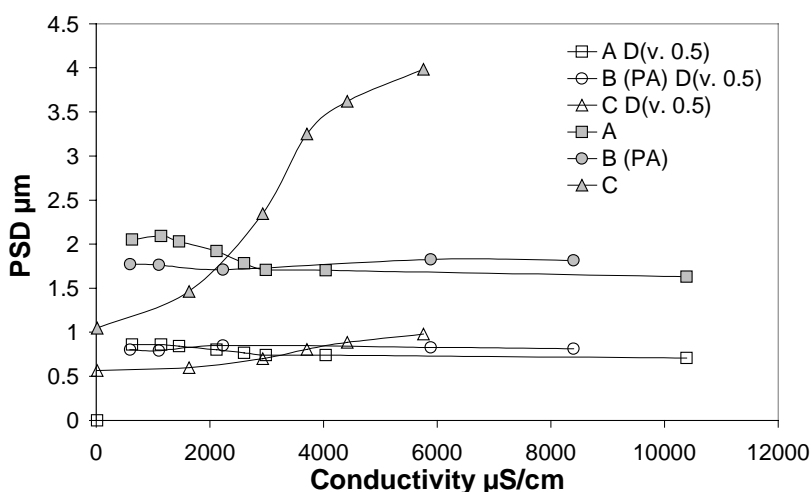
Dispersions A and B with PA could be stirred up to 2000 rpm for 30 minutes without agglomeration. Dispersion C was slightly agglomerated after 15 minutes, table 3.

The colloidal stability was tested in the conductivity range of 0.020–10.2 mS/cm. The dispersions stabilized with starch were unaffected, while C was slightly affected at conductivity levels above 2000  $\mu\text{S}/\text{cm}$ , figure 5.

The conclusion is that the dispersions showed good to excellent colloidal stability in high levels of shear and electrolyte concentration.

**Table 3.** Particle size of AKD dispersions at different shear times. D (v. 0.5) and D (v. 0.9) represent the volume weighted particle size which 50 % and 90 %, respectively, of the sample is below.

Time of stirring at 2000 rpm BDDJ minutes	Dispersion A D(v. 0.5)/D(v. 0.9) $\mu\text{m}$	Dispersion B with PA D(v. 0.5)/D(v. 0.9) $\mu\text{m}$	Dispersion C D(v. 0.5)/D(v. 0.9) $\mu\text{m}$
0	0.6/1.1	0.6/1.4	0.6/1.7
15	0.5/1.0	0.6/1.3	0.8/2.2
30	0.5/1.0	0.6/1.5	0.8/3.7
45	0.5/1.0	0.9/7.8	1.0/4.8

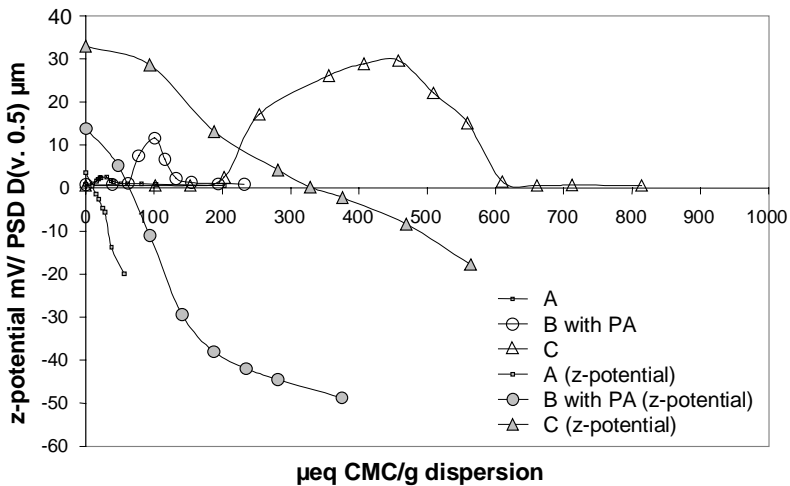


**Figure 5.** The volume weighted particle size measured at different conductivity levels. The experiments were performed in a BDDJ at pH 7, 1000 rpm for 60 seconds.

#### 4.1.2 Influence of polyelectrolytes and surfactants

Two different polyelectrolytes were used in the study, CMC, and birch wood xylan. They were selected to investigate how a high charge density versus a low charge density polymer affects the colloidal stability. The charge density was 3.6 meq/g for CMC and 0.50 meq/g for xylan.

All three dispersions lost their colloidal stability in presence of CMC, figure 6. As expected dispersion A with the lowest charge density agglomerates at a lower concentration of CMC than B with PA and C. Dispersion C with the highest charge density was not affected until high addition levels. The agglomeration was induced at CMC additions bringing the z-potential close to zero. Further information that can be found in figure 6 is that dispersions with a high surface charge are able to form larger agglomerates due to a larger number of connecting points on the surface of the AKD particles.

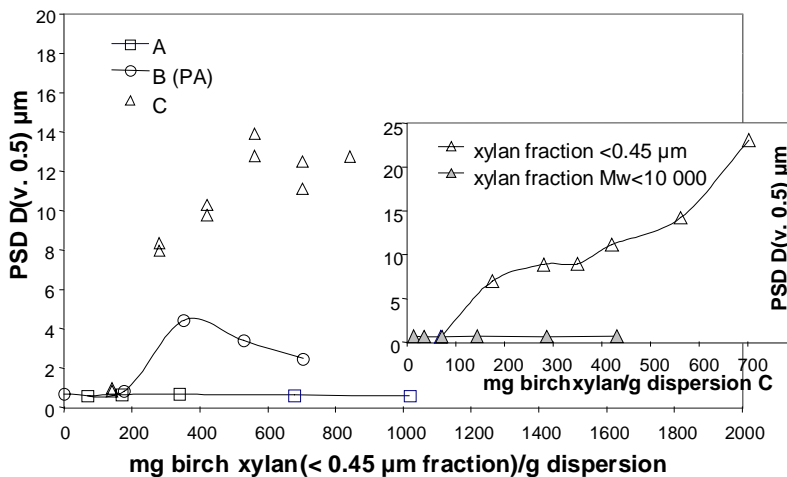


**Figure 6.** Influence of CMC on the colloidal stability of AKD. The experiments were carried out in a BDDJ at pH 7, 1000 rpm for 60 seconds.

Xylan did not affect the stability as efficiently as CMC, figure 7. Only the medium and high charge density dispersions did flocculate. A reason of why dispersion A did not flocculate could be that the cationic starch in A has a too low charge density to interact with xylan, while B with PA and C have a high enough surface charge to interact. A low charge density polyelectrolyte requires a high charge density of the opposite polyelectrolyte to interact. Otherwise it is more favorable to interact with counterions in the solution and maintain a high degree of mobility.

The xylan test indicates that AKD dispersions stabilized with a high charge density polyelectrolyte can be more sensitive to flocculation than dispersions stabilized

with a low charge density polyelectrolyte in white water systems containing high concentrations of low charge density anionic components.

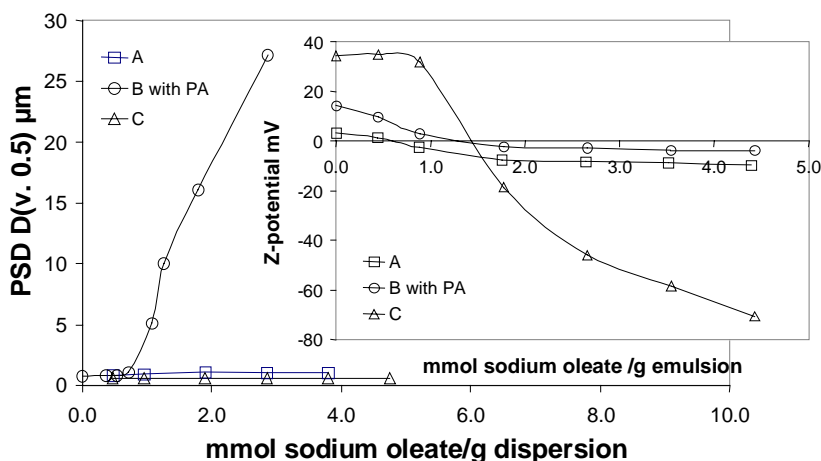


**Figure 7.** Influence of birch xylan on the colloidal stability of AKD. Two different fractions of xylan (<0.45 μm and Mw <10 000) were used. Tests were performed in a BDDJ, at pH 7, 1000 rpm for 60 seconds.

Sodium oleate was used as a model substance for surfactants. Surface active compounds such as fatty acid soaps originate from the wood extractives. Surfactants are also occasionally added into the paper machine to overcome problems with foaming.

In this test the influence of sodium oleate in presence of air bubbles was tested using the BDDJ. The sodium oleate concentration was varied between 0–0.40 mM and the stirring speed was 1000 rpm for 60 seconds. The influence of sodium oleate in absence of air bubbles was tested in a cylinder with a screen-plate. The screen-plate was used for stirring the sample. The liquids in the samples were degassed prior to testing, for a detailed description of the experimental design see Paper I.

Figure 8 shows the results when the influence of sodium oleate was tested in the absence of air bubbles. The z-potential for all three dispersions decreases with an increasing amount of sodium oleate. This indicates that oleate is adsorbed on the AKD particles and flocculation can occur due to hydrophobic interactions. Flocculation could also be induced by charge neutralization. No flocculation was observed for dispersions A and C, even though oleate was adsorbed. Explanations of why these dispersions were not affected could be that A is stabilized sterically or that there is not enough adsorbed oleate molecules present to promote flocculation. The z-potential for dispersion C changes very rapidly around zero, which makes it difficult to add the exact amount of oleate to induce flocculation.



**Figure 8.** Influence of sodium oleate on colloidal stability of AKD in the absence of air bubbles at pH 7. The experiments were carried out in a graduated cylinder with a circular screen plate. The samples were stirred for 60 seconds.

When air bubbles were present dispersions B with PA and C did flocculate. For C there was a strong flocculation compared to the case with no air bubbles (figure 8 in Paper I). The presence of air bubbles introduces air/water interfaces to the system, which might interact with the AKD particles heavily covered with oleate such that the electrostatic repulsion between the AKD particles is overcome.

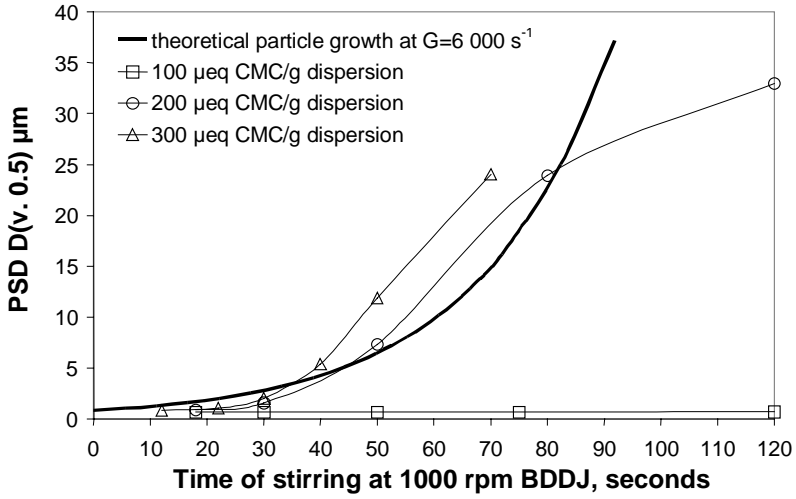
Flocculation induced by surfactants can be very sensitive to different conditions in the white water e.g. pH. Changing pH from 7, at which pH most experiments were done, to 8 drastically changed the stability for one of the dispersions, figure 9 in Paper I.

The results of this part clearly indicate that anionic polymers and surfactants existing in a white water system can cause agglomeration of AKD dispersions.

#### 4.1.3 Kinetics of AKD flocculation

The obtained results show that agglomeration occurs in presence of anionic polymers and surfactants in a fiber free environment. But if fibers and fines are present, can AKD flocculation occur on a time scale that competes with deposition onto the fibers and fines.

The kinetics of AKD flocculation was studied experimentally by measuring the average particle size of dispersion C at different stirring times and CMC additions. The results showed that an appreciable aggregation (an average size of 2.5  $\mu\text{m}$  in diameter) was obtained after 25 seconds, figure 9.



**Figure 9.** Mean particle size of single particles/agglomerates of AKD (dispersion C) at different concentrations of CMC and stirring times (1000 rpm). The theoretical particle growth with time was calculated assuming a uniform shear of  $6000 \text{ s}^{-1}$ .

The agglomerates reached a maximum average size of approximately  $25 \mu\text{m}$  before they were affected by the shear. Figure 9 also includes the results of theoretical calculations of the particle growth as function of time. The theoretical calculations are based on a model for orthokinetic collisions between spherical particles in uniform shear with corrections for the collision efficiency [25–26]:

$$-\ln(N/N_0) = K N_0 \alpha_{Sh} t \quad K = 4/3G(a_1 + a_2)^3 \quad (4)$$

where  $N_0$  is the initial number of particles,  $N$  is the number of particles at time  $t$ ,  $K$  is the rate constant and  $\alpha_{Sh}$  is the collision efficiency constant. The rate constant  $K$  is given by the uniform shear rate,  $G$ , and the radii,  $a_1$  and  $a_2$ , of the particles involved in the collision.

The collision efficiency constant was calculated according to Han et al. [26], and this factor includes the effects of hydrodynamic repulsion and van der Waals attractions. The hydrodynamic repulsion exists since the water between particles has to be moved out of the way before the collision can take place. It is therefore more difficult for a small particle to collide with a large particle, since the small particle would rather follow the streamlines around the large particle than collide. The theoretical calculations of particle growth with time give a good estimate of the observed flocculation rate.

Encouraged by this good agreement, the same type of calculation was performed to calculate the AKD deposition time for fibers and fines in typical white water conditions. In this calculation a hydrodynamic radius of  $30 \mu\text{m}$  was used for fibers [25] and two different radii for fines, 1 and  $2 \mu\text{m}$ . The fiber concentration was

assumed to be  $4.75 \text{ kg/m}^3$ , the fines concentration to be  $0.25 \text{ kg/m}^3$ , the AKD dispersion concentration to be  $0.01 \text{ kg/m}^3$  and the radius of the AKD particles to be  $0.40 \text{ }\mu\text{m}$ . The calculation was made at two different shear levels 100 and  $6000 \text{ s}^{-1}$ . The estimated times for flocculation and deposition are shown in table 4.

**Table 4.** Theoretical estimates of flocculation and deposition times.

	Size ratio	$t^{1/2}$ seconds $G=100 \text{ s}^{-1}$	$t^{1/2}$ seconds $G=6\ 000 \text{ s}^{-1}$
AKD/AKD	1	800	30
AKD/Fines ( $1\ \mu\text{m}$ )	0.4	100	10
AKD/Fines ( $2\ \mu\text{m}$ )	0.2	2 000	200
AKD/Fibers ( $30\ \mu\text{m}$ )	0.01	50 000	900

Although the calculation contains simplifications e.g. that the fiber and fines have a smooth surface with no protruding fibrils the result of the calculation clearly indicates that AKD flocculation occurs on the same time scale as deposition to fibers and fines. The result also indicates that the deposition to fines is faster than to fibers. Fines are apparently important for the retention of AKD.

## 4.2 Migration of AKD

Paper II considers the migration of AKD. Many authors have discussed the mechanism of AKD spreading in the literature. Earlier studies [9–10] proposed that AKD spreads on cellulose to a molecular monolayer or thin multilayer. Shen et al. [14] proposed that spreading of AKD melt is limited, and vaporization and re-deposition of AKD most likely drives the migration. In the papers discussed so far, the spreading of AKD has been studied on model surfaces at temperatures above the melting point of the AKD wax. There have been very few reports about the influence of extractives on the migration of AKD. It was suggested that sodium oleate could prevent the AKD spreading and thereby also the reaction with cellulose and the sizing efficiency [15].

The objective of this paper was to investigate the migration of AKD through paper sheets and also through sheets containing extractives. If the migration of AKD is effective, uniform distribution of AKD is less crucial to achieve an efficient sizing. The AKD used in the study had a melting point of  $52\text{--}53 \text{ }^\circ\text{C}$ . The AKD migration was studied through sheets impregnated with abietic acid, betulinol, sodium oleate and tripalmitine. The migration was studied at two different temperatures,  $80 \text{ }^\circ\text{C}$  and  $105 \text{ }^\circ\text{C}$ .

### 4.2.1 AKD migration

The first part of the investigation was focused on AKD migration through papers of different thickness, 130, 230 and  $320 \text{ }\mu\text{m}$ . The sheets were laboratory sheets made

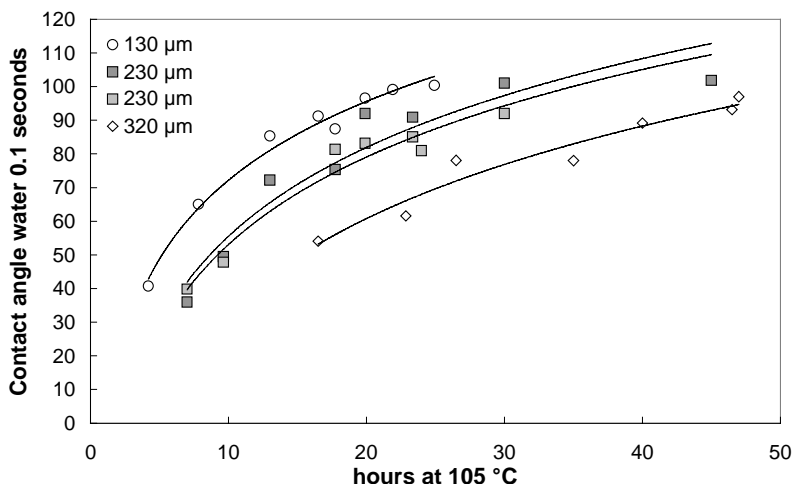
from ECF bleached pulp with an extractive content less than 0.1 %. The porosity and the thickness of the papers used are shown in table 5.

**Table 5.** Grammage, air permeance and thickness of the laboratory sheets. The figures in parentheses are the coefficients of variation expressed in %.

Grammage g/m <sup>2</sup>	Air Permeance ml/min	Thickness µm
70	1870 (6)	130 (4)
140	851 (11)	227 (4)
210	534 (10)	322 (4)

The experimental setup for studying the AKD migration is described under section 3.2.3 “Migration of AKD”. The AKD impregnated papers used in the study had an AKD content of 86 mg/g. The diffusion through the sheets was characterized by the time required to reach a contact angle of 90°.

AKD migration through a paper with a thickness of 130 µm was reached after 17 hours, through 230 µm after 25 hours, and through 320 µm after 42 hours at 105 °C, figure 10.



**Figure 10.** The contact angles (water) as a function of storage time at 105 ± 2 °C measured on samples with three different thickness in contact with AKD impregnated paper. The samples were made by mounting untreated papers strips (130, 230 and 320 µm thick) on top of AKD impregnated paper strips.

The diffusion coefficient for AKD migration at 105 °C could be roughly estimated from the results in figure 10. The diffusion coefficient was calculated from the isothermal curves for each separate thickness according to the expression:

$$15z = (2Dt)^{1/2} \quad (5)$$

where  $z$  is the thickness of the sheet,  $t$  the diffusion time and  $D$  the diffusion coefficient. Equation (9) is based on Einstein's equation treating the Brownian motion as a one-dimensional random walk. The factor of 15 corrects for the tortuosity of the diffusion path in the sheet [27].

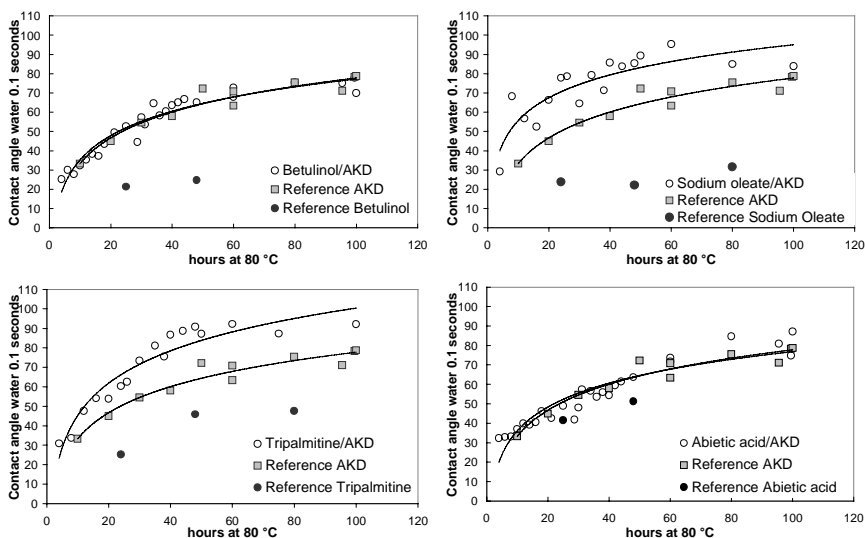
The diffusion coefficient for AKD obtained from figure 10 is  $10^{-11} \text{ m}^2/\text{s}$  at 105 °C. Seppänen et al. [13] estimated the diffusion coefficient to be of the same order of magnitude,  $10^{-11} \text{ m}^2/\text{s}$ , at a temperature of 50 °C.

#### 4.2.2 Influence of extractives on AKD migration

To study the influence of extractives on AKD migration, migration through sheets impregnated with extractives was observed. The extractive content and the surface energy of the impregnated papers are presented in table 6. The surface energy was measured to assure that the content of the individual extractives was sufficient to significantly change the surface properties of the impregnated sheets. The temperature in the experiments was 80 °C, which is a realistic choice considering the temperature in jet-rolls.

**Table 6.** The content of extractives in the impregnated papers determined by chemical analysis (solvent extraction and capillary gas chromatography). The surface energy was determined by contact angle measurements. \*\*\* Sodium oleate is soluble in water and consequently the surface energy of the sodium oleate impregnated sheets could not be determined.

Impregnated papers (130 µm)	Content of impregnating agent mg/g	Surface energy mN/m
Untreated	—	53
10 % AKD	86	31
Abietic acid	18	37
Betulinol	24	44
Oleate	2.5	***
Tripalmitine	4.8	35



**Figure 11.** AKD migration through sheets impregnated with extractives. The migration was studied by measuring the contact angles (water) on samples stored for different times at 80 °C. The samples consisted of a paper impregnated with an extractive (130  $\mu\text{m}$ ) mounted in between an untreated (130  $\mu\text{m}$ ) and an AKD impregnated paper. Two kinds of reference samples were measured: (Reference AKD) two untreated (130  $\mu\text{m}$  each) paper strips on top of an AKD impregnated paper strip and (Reference extractive) an untreated paper strip (130  $\mu\text{m}$ ) on top of a strip impregnated with extractive.

Figure 11 shows the diffusion rate of AKD through the impregnated paper sheets and the reference samples, (Reference AKD) and (Reference extractive).

The reference samples containing extractives were aimed to show the migration of the extractives themselves.

The results show that betulinol itself does not migrate and that the migration rate for AKD through the betulinol impregnated sheets is approximately the same as in the reference sample (Reference AKD). Sodium oleate does as expected not migrate and there are no indications that sodium oleate should influence the migration of AKD, at least at the concentration used in the study. For tripalmitine itself there might be a slight tendency to migrate through the sheet but there is no indication that tripalmitine negatively affect the AKD migration.

For abietic acid the results clearly indicate, eventhough there were few reference samples made, that abietic acid migrates approximately as fast as AKD. It is therefore not possible to conclude if migration of AKD or abietic acid or a combination of them both caused the observed hydrophobicity.

Migration of AKD through sheets containing oleic acid was also studied (results are not shown). As expected these results showed that oleic acid migrates faster than AKD, no conclusions of the influence on the AKD migration could thus be made.

If the migration of AKD in our experiment occurs by a macroscopic migration, it would be expected that the extractives interfered with the spreading. Therefore it seems reasonable to assume that the spreading occurs by a diffusion process. If this diffusion process take place via the vapor phase [14] or via surface diffusion [13] has not been addressed. The focus of these experiments is entirely on the influence of extractives on the AKD migration. The effect of a possible reaction between AKD and cellulose on the migration has not been considered.

There were no indications in Paper II that extractives such as betulinol, oleate and tripalmitine interfere with the migration of AKD, and the diffusion coefficient for AKD migration in paper was estimated to be of the magnitude of  $10^{-11}$  m<sup>2</sup>/s at 105 °C.

### 4.3 Pre-flocculation and internal sizing with AKD agglomerates

The main objective of the work in Paper III was to use AKD agglomerates for sizing. The tendency for the dispersions to flocculate in white water and the shear stability of the formed agglomerates were also investigated.

If AKD agglomerates should be used for sizing, an important question to answer is how far the agglomerates can be placed from each other and still produce a sufficient sizing. As seen in Paper I, AKD agglomerates could be up to 30 µm in diameter (volume weighted average size). It is not difficult to see the advantage of using agglomerates for size retention. Microphotographs of unflocculated and flocculated dispersions are shown in figure 12

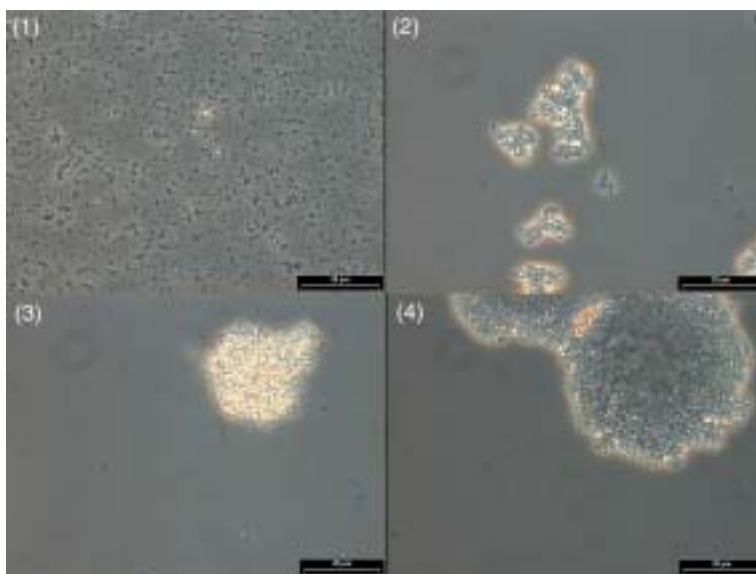
#### 4.3.1 Flocculation in white water

The ability of the AKD dispersions to flocculate in white water was studied under shear in a BDDJ by measuring the particle size distribution. The colloidal stability was tested at various concentrations of white water, where the white water was diluted in deionized water in the range of 0–100 % (v/v). The samples were stirred at 1000 rpm for 60 seconds, sodium sulphate was added to maintain the conductivity level, 1100 µS/cm.

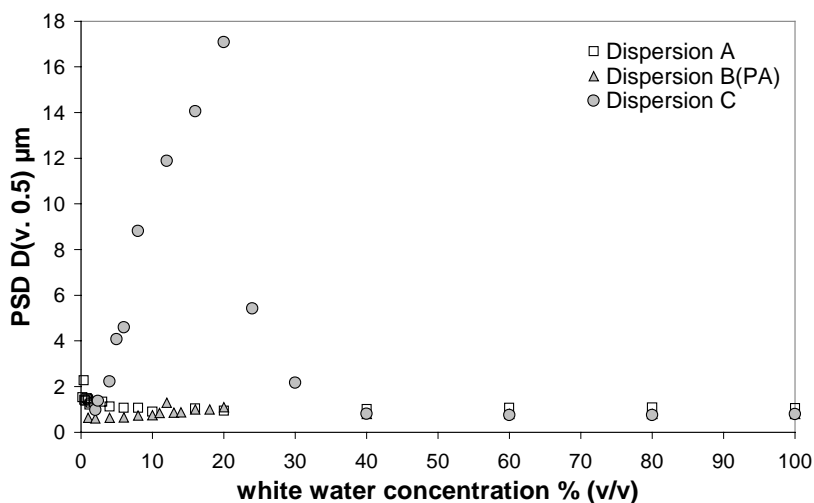
The white water samples used in the study were collected from the wire pit of a paper machine producing bleached linerboard. The samples were cooled to room temperature and then filtered through a 0.45 µm membrane. The white water samples collected on different occasions showed a large variation see table 7.

**Table 7.** Chemical analysis of filtered white water samples. The white water samples were collected from the wire pit during the production of linerboard and filtrated through a 0.45 µm membrane, pH 7.4 - 7.6, 1000 - 1200 µS/cm.

White water fraction	Total amount of carbohydrates mg/l	Total amount of lignin mg/l	COD mg/l	Cationic demand µeq/l
0.45 µm	120-170	12-30	290-510	30-190



**Figure 12.** Optical microphotograph of (1) dispersion A unflocculated, (2) dispersion A flocculated with CMC, (3) dispersion B(PA) flocculated with CMC and (4) dispersion C flocculated with CMC. The bar corresponds to 20  $\mu\text{m}$ .



**Figure 13.** Particle size as a function of different concentrations of white water. The white water (filtered through 0.45  $\mu\text{m}$ , 190  $\mu\text{eq/l}$ , 1100  $\mu\text{S/cm}$ , pH 7.5) was diluted with deionized water and sodium sulphate was added to maintain a conductivity of 1100  $\mu\text{S/cm}$ . The AKD dispersion concentration was 75 mg solids content / l. The tests were made in a BDDJ, 1000 rpm, 60 seconds.

Eventhough the white water samples differed, they all had the ability to induce flocculation of dispersion C although a larger amount of the white water with the lowest cationic demand was required to induce flocculation. The AKD agglomerates formed in white water did not reach the same size as the agglomerates formed with CMC. Dispersion C formed agglomerates reaching a diameter of approximately 15  $\mu\text{m}$  while flocculation of A and B(PA) was not observed, figure 13. The reason why flocculation was not observed is probably that they have a too low surface charge to interact with the anionic polymers in the white water. These results agree well with the results found in Paper I.

#### **4.3.2 Shear stability of AKD agglomerates**

In order to survive in a paper machine the agglomerates must be able to tolerate high levels of shear. The two kinds of AKD agglomerates (formed by flocculating dispersion C with CMC or white water) were stirred at 2000 rpm up to 80 minutes. A shearing speed of 1000 rpm in a BDDJ corresponds to a maximum shear rate of 6000  $\text{s}^{-1}$  [28].

The shear stability of both types of agglomerates was excellent. There was no indication of re-dispersing during the 80 minutes they were exposed to high shear, see figures 3 and 4 in Paper III.

The shear stability was also confirmed in the dynamic sheet former. There was no breakup observed eventhough the fiber stock was pumped under high shear through a narrow nozzle onto the mesh placed on a rotating drum.

#### **4.3.3 Internal sizing with pre-flocculated AKD dispersions**

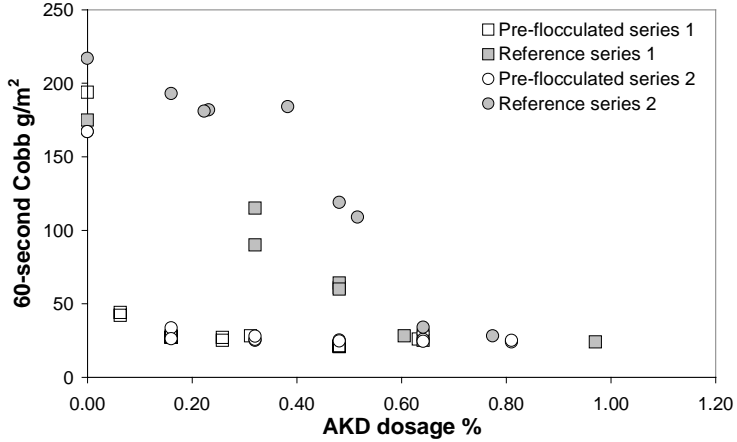
The laboratory sheets were made from TCF bleached hardwood pulp in a dynamic sheet former. The sheets were sized by adding a pre-flocculated dispersion into the fiber stock. Pre-flocculation was accomplished by flocculating dispersion C by using either CMC or white water.

Sizing with pre-flocculated AKD using CMC as a flocculating agent was performed on two separate occasions, series 1 and 2, figure 14. The sizing efficiency measured by 60-second Cobb was much higher using pre-flocculated AKD than using unflocculated dispersion (reference series).

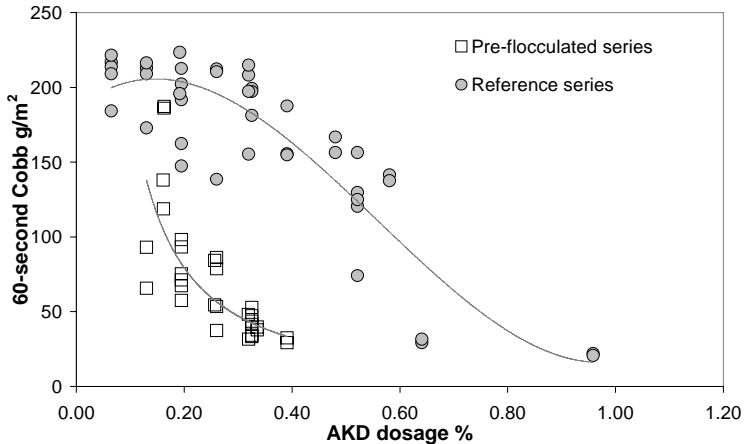
Sufficient sizing with pre-flocculated AKD was reached at a dosage of 0.16 %, one fourth of the unflocculated addition level. A sufficient sizing is here defined as a 60-second Cobb of 30  $\text{g}/\text{m}^2$ .

Sizing with pre-flocculated AKD using white water as a flocculating agent was also performed, figure 15. Here a sufficient sizing was reached at dosage level of 0.40 %. The AKD agglomerates did not reach the same size when using white water ( $\sim 15 \mu\text{m}$ ) as a flocculating agent as when using CMC ( $\sim 30 \mu\text{m}$ ). This could be an explanation of why the sizing efficiency was lower with agglomerates formed with white water.

The addition levels of AKD used here to reach a 60-second Cobb of 30 g/m<sup>2</sup> are much higher than the dosages required for a commercial paper machine. This is expected since the sheets were made in a dynamic sheet former which has a low retention. It must be remembered that no retention aids were used when making the laboratory sheets.



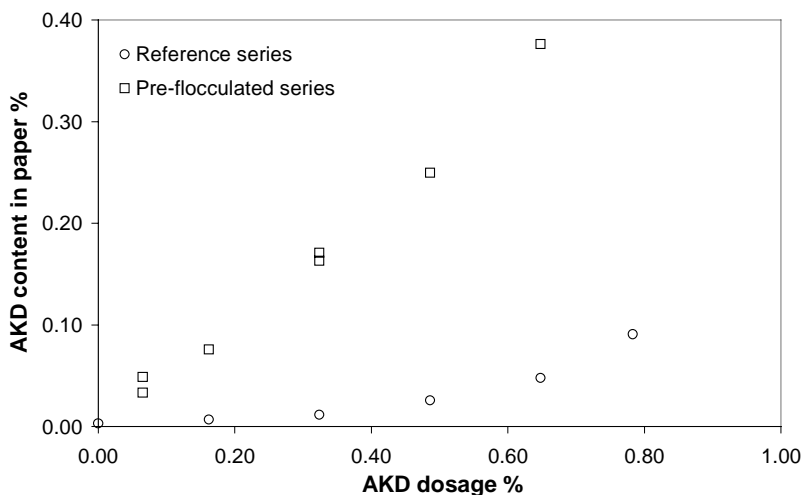
**Figure 14.** 60-second Cobb values of laboratory sheets (dynamic sheet former) as a function of AKD dosage. The sheets were sized with pre-flocculated AKD and unflocculated dispersions (reference). Pre-flocculation was performed with CMC. Dispersion C was used in the series. The AKD dosage in % refers to the AKD wax content. The sheets were conditioned overnight before the Cobb measurements.



**Figure 15.** 60-second Cobb values of laboratory sheets (dynamic sheet former) as a function of AKD dosage. The sheets were sized with pre-flocculated AKD and unflocculated dispersions (reference). Pre-flocculation was made with white water. Dispersion C was used in the series. The AKD dosage in % refers to the AKD wax content. The sheets were conditioned overnight before the Cobb measurements.

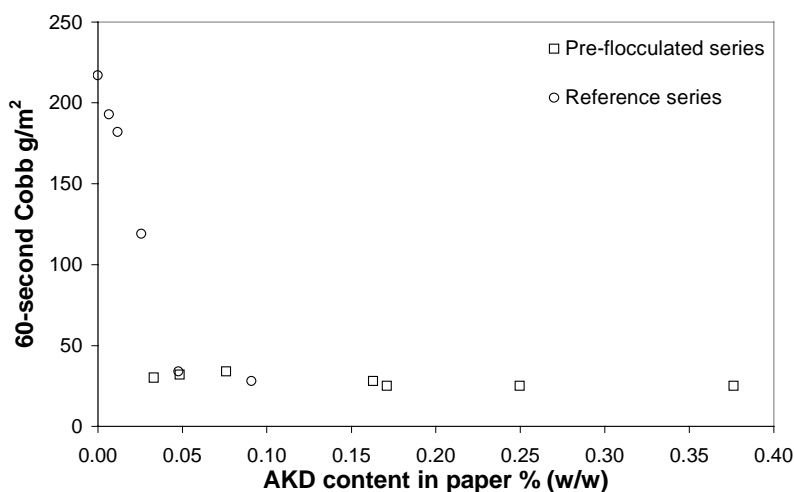
The sizing efficiency was also evaluated by contact angle measurements with water. The results of the contact angle analysis confirmed the results already observed with 60-second Cobb, see figure 7 in Paper III.

The AKD content in the laboratory sheets was also determined by using alkaline hydrolysis followed by solvent extraction and quantification with capillary gas chromatography. The quantitative analysis shows that the higher sizing efficiency obtained with pre-flocculated AKD is explained by a higher retention of the agglomerates, figure 16.



**Figure 16.** The total AKD content in laboratory sheets (dynamic sheet former) as a function of AKD dosage. The total AKD content was determined by solvent extraction and GC analysis. The laboratory sheets were sized with pre-flocculated and unflocculated dispersions. Pre-flocculation was done with CMC. Dispersion C was used in the series. The sheets were conditioned overnight and then wrapped in aluminum foil and analyzed after 3 weeks. The AKD dosage in % refers to the AKD wax content.

As mentioned earlier, an interesting question is how far the AKD agglomerates can be placed from each other and still produce a sufficient sizing. This question was not investigated specifically in this paper. The result in figure 17 shows, however, that an AKD content of 0.05 % corresponds quite well to a Cobb value of 30 g/m<sup>2</sup>, no matter if the laboratory sheets were sized with unflocculated or pre-flocculated dispersion. Apparently, the spreading of AKD agglomerates is sufficient for sizing.



**Figure 17.** 60-second Cobb values of the laboratory sheets (dynamic sheet former) as a function of the total AKD content in the sheets (solvent extraction /GC analysis). The laboratory sheets were sized with pre-flocculated and unflocculated dispersions (reference). Pre-flocculation was made with CMC. Dispersion C was used in the series. The sheets were conditioned overnight and then wrapped in aluminum foil and the AKD content was analyzed after 3 weeks. The AKD dosage in % refers to the AKD wax content.

Assuming, in accordance with the results, that 0.05% is sufficient for sizing, the distribution of AKD particles can be estimated. The outer surface of fibers is assumed to be  $1 \text{ m}^2/\text{g}$ , the diameter of the particles to  $0.80 \text{ }\mu\text{m}$  and the density of the AKD to  $960 \text{ kg}/\text{m}^3$ . If the particles were uniformly distributed over the fiber surface ( $1 \text{ m}^2$ ) they would be deposited at an average distance of  $20 \text{ }\mu\text{m}$ .

In a flocculated dispersion with agglomerates containing 1000 AKD particles the average distance would be  $600 \text{ }\mu\text{m}$ , according to this simple calculation. Agglomerates containing 100 and 10 000 particles would have an average distance of 200 and  $2000 \text{ }\mu\text{m}$  respectively. The number of AKD particles in a floc with a diameter of  $30 \text{ }\mu\text{m}$  is not known, but a reasonable number is about 1000. The aggregates did not appear to be dense and they contained a large amount of water. It seems very reasonable that sizing is obtained when the particles are distributed at a distance of  $20 \text{ }\mu\text{m}$ , considering that the particles will relax to their low equilibrium contact angle [12]. It could appear more surprising that sizing was achieved using pre-flocculated dispersion, considering that the agglomerates are deposited hundreds of microns apart. However in Paper II, the diffusion coefficient for AKD was estimated to be  $10^{-11} \text{ m}^2/\text{s}$ . Seppänen et al. [13] came to the same magnitude when studying the AKD migration on silica surfaces. Using the estimated surface diffusion coefficient for calculating the AKD migration, it is found that AKD spreads about  $500 \text{ }\mu\text{m}$  in 6 hours. This indicates that spreading over 6 hours is

sufficient to obtain sizing even if the AKD agglomerates are separated by some hundred microns.

The findings in Paper III clearly indicate that agglomerates of AKD can be used for internal sizing. The flocculation of AKD must of course be carefully controlled and the suggestion is that the size dispersion is flocculated prior to addition into the fiber stock. The question if a pre-flocculation process could give rise to problems with scaling and spots in the produced paper has not been addressed in this paper. It was also shown in this paper that AKD dispersion could agglomerate in real white waters.

## **5. Conclusions**

Hopefully the results obtained in this thesis will contribute to a better understanding of the function of AKD dispersions in the internal sizing process. The results have shown that AKD dispersions can flocculate in real white water systems. AKD dispersions produced for wet-end systems with a high cationic demand can be less colloiddally stable than dispersions emulsified with low charge density cationic starch. AKD flocculation occurs on the same time scale as deposition of AKD particles onto fines and fibers, and should be a process to consider during papermaking.

The findings in this work show that agglomeration should not merely be seen as a negative process. The sizing efficiency, due to increased retention, was significantly improved using agglomerated AKD for internal sizing. The conventional picture that the sizing agents must be uniformly distributed to achieve efficient sizing could be questioned based on the results in this thesis.

Though the work has been focused on AKD dispersions, the results concerning the colloidal stability and sizing with pre-flocculated dispersions should be possible to transfer to other sizing systems. The emulsification of rosin and ASA are based on the same principles as for AKD. Agglomeration of size dispersions during production could be achieved by developing new dosage strategies, for instance by premixing cationic size dispersions with retention aids such as anionic colloidal silica or polyacrylamide.

The results obtained in this thesis have shown that alternative modes of internal sizing can be possible and the process of using pre-flocculated AKD for internal sizing is the subject for a patent application.

## 6. Acknowledgements

First of all I would like to thank AssiDomän AB, Eka Chemical AB and Kappa Kraftliner Piteå for supporting this project financially and my manager Britt - Mari Antti for the opportunity and her support. I will of course under “first of all” also express my deepest gratitude to my supervisor Lars Ödberg who has supported me unconditionally with a never ending enthusiasm, his numerous of ideas and improvements. Also my examiner Johan Sterte for invaluable comments and criticism and his strong support and finally for housing me at his division Chemical Technology. A huge thanks to my co-author Dan Lindström for his optimistic support combined with an invaluable help.

I will extend my warmest thanks Johan Landfors and to the members in the reference group for the support and encouragement: Kjell Andersson, Maria Göransson, John Nicholass, Ola Karlsson, Michael Persson and Mirjam Sterner.

Special thanks will also go to Pavol Barla, Janne Laine, Jan Lidén, Erik Lindgren and Agne Swerin for valuable discussions in the paper chemistry field.

I will also direct my special thanks to Ruth Dunleavey for preparing the dispersions and Ralf Dürholz for taking the optical microphotographs.

My warmest thanks go to Ann-Cristine Bäckman, Lennart Esterud, Lena Hansson, Margareta Lind, Andreas Marklund, and Ulf Norberg for their skilful assistance.

I am very grateful to Billerud Skärblacka for lending me the Malvern instrument.

I would like to send my deepest gratitude to Ingemar Berglund for the linguistic revision, domo arigato gozaimashita!

Special thanks to all my colleges at Kappa Kraftliner Piteå and the Department of Chemical and Metallurgical Engineering for creating such creative and pleasant climate.

A special thanks to Monica Berglund for her for consolingly words she never changed during the whole project - Du har ju två år på dig!

Finally I wish to thank my family for their deep interest and love and especially to Klas and Michael. Vad jag är glad att ni finns i mitt liv, pojkar!

A few mentioned, nobody forgotten.

## 7. References

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