Norwegian University of Science and Technology

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# **Colloidal wood resin: Analyses and interactions**

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# Preface

The work presented here has been carried out at the Norwegian Pulp and Paper Research Institute (PFI) and the Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU) under supervision of Associate Professor Størker Moe (NTNU). Dr Janne Laine (Helsinki University of Technology) has been the co-supervisor. Norske Skog ASA, Nordic Industrial Fund and the Research Council of Norway provided the funding.

This thesis is a summary of the following papers, referred in the text by their Roman numerals. Some additional data is also presented, especially regarding effects of fines and colloidal wood resin in laboratory sheets. This data is also found in the supporting publications.

- I. Mosbye, J., Harstad, B. and Fiksdahl, A. (2000): Solid phase extraction (SPE) of hydrophobic components from a model white water, Nordic Pulp Paper Res. J. 15(2), 101.
- II. Mosbye, J. Moe, S. and Laine, J. (2002): The charge and chemical composition of fines in mechanical pulp, Nordic Pulp Paper Res. J. 17(3), 352.
- III. Moe, S.T. and Mosbye, J. (2003): Swelling of mechanical pulp fines after chemical treatment, 12th Int. Symp. Wood Pulping Chem., Madison, 5.
- IV. Mosbye, J., Laine, J. and Moe, S. (2003): The effect of dissolved substances on the adsorption of colloidal extractives to fines in mechanical pulp, Nordic Pulp Paper Res. J. 18(1), 63.
- V. Mosbye, J., Moe, S., Tammelin, T., Saarinen, T. and Laine, J. (2003): The ability of PEO to remove model colloidal extractives from solutions with different types of fines, submitted to Nordic Pulp Paper Res. J.
- VI. Mosbye, J., Foss, M. H., Laine, J. and Moe, S (2003): Interaction between model colloidal wood resin, fillers and dissolved substances, Nordic Pulp Paper Res. J. 18(2), 194.

#### Supporting publications, not included in the papers above

- VII. Hoel, H. and Mosbye, J. (1997): Colloidal and dissolved TMP removals by inorganic "trash" catchers, 9<sup>th</sup> Int. Symp. Wood Pulping Chem., Montreal, P1-1.
- VIII. Mosbye, J., Holte, M., Laine, J. and Moe, S. (2001): Adsorption of model colloidal extractives to different types of fines, 6<sup>th</sup> Res. Forum on Recycling, Magog, 139.
- IX. Krogerus, B., Eriksson, L., Sundberg, A., Mosbye, J., Ahlroth, A., Östlund,
  I. and Sjöström, L (2002): Fines in closed circuits final report, SCAN
  FORSK report 740.
- Mosbye, J., Lyngstad, H. and Thomassen, B. (2002): The combined effect of fines and wood resin on paper surface and strength, SCAN FORSK report 742.

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# Abstract

This thesis presents studies of the interactions between suspended particles and dissolved and colloidal substances (DCS) in process water. The main focus has been to determine if colloidal wood resin is adsorbed by suspended fines or fillers, and how the dissolved material influences this adsorption. The effect of some synthetic polymers on this adsorption has also been investigated.

Successive refining of mainly Norway spruce followed by removal of the produced fines after each refining stage, resulted in fines with different physical and chemical properties. In the first refining stage mainly flake-like fines were produced, while more fibrillar fines were produced in later refining stages. The different types of fines were analysed for both the bulk and the surface composition. Variation in the chemical composition between the fines was particularly striking with regard to the surface composition. Special attention was also given to the amount and origin of charged groups since these may consume cationic additives in the papermaking process. After alkali treatment, between 80 and 90% of all the charged groups measured by polymer adsorption originated from three uronic acids.

Fines were shown to adsorb model colloidal wood resin, but the adsorption was greatly influenced by the pH or salt content. Also the amount of dissolved components in the suspension, which sterically stabilised the colloidal wood resin, was shown to strongly influence the adsorption of the colloidal wood resin to the fines. The flake-like fines adsorbed the colloidal wood resin to a higher extent than the fibrillar fines. This selectivity was also possible to obtain by using polyethyleneoxide (PEO). PEO removed the sterically stabilised colloidal wood resin more efficiently when flake-like fines rather than fibrillar fines were present. For comparison, cationic polyacrylamide (CPAM) did not have this selectivity. The selectivity of PEO was explained by a higher affinity to flake-like fines than fibrillar fines. It was shown that more PEO adsorbed to flake-like fines rather than to fibrillar ones. PEO may adsorb to extractive surfaces, but was inhibited by adsorbed components from the dissolved fraction. The degree of stabilisation was also shown to influence the adsorption of the colloidal wood resin by other particles like fillers. This adsorption, which was energetically favourable, did not occur at high concentrations of dissolved material.

# Keywords

Adsorption, charged groups, colloidal wood resin, dissolved substances, extractives, fillers, fines, mechanical pulp, Norway spruce, PEO, polyethyleneoxide, solid phase extraction, SPE, steric stabilisation, surface composition, surface energy, swelling, uronic acids

# Introduction

There are two main ways of producing papermaking fibres from wood. In chemical pulping the fibres are separated in a digester after the addition of different chemicals and in mechanical pulping the separation is done by mechanical means. During the mechanical pulping, stiff fibres and fibre fragments are produced. The latter are usually referred to as "fines". Mechanical pulp is primarily used to produce different grades of board and printing paper, sometimes collectively referred to as "wood containing paper". Examples of such paper grades are newsprint paper, super calendered (SC) paper and lightweight-coated (LWC) paper.

Prior to the start of papermaking, the mechanical pulp is suspended in process water and different components are subsequently released into the water. Some of this material may dissolve, like simple salts or carbohydrates, while hydrophobic material like wood resin may be dispersed as colloidal droplets. This material is called dissolved and colloidal substances (DCS), and may interact with itself or the suspended pulp in different ways. Many different components may be added to this mixture and are often called "additives". Examples of groups of such components are fillers, retention aids, fixatives and additives to improve strength.

The interactions between these fibres, fines, DCS and additives are complex and difficult to predict. Some of these interactions are wanted, like the retention of small particles or agglomerates to the fibre web during the forming of the paper. Such interactions may be enhanced by the addition of polymers which are often termed fixation- or retention aids when used for this purpose. Other interactions are unwanted, like the adsorption of colloidal hydrophobic material to process equipment resulting in *e.g.* deposition inside pipelines or plugging of the wire. As the paper industry is moving towards reduced freshwater consumption, and thus potentially creating higher concentrations of DCS, knowledge of the interactions between suspended particles and DCS becomes important. The science that addresses these matters is called "wet end chemistry" or "process water chemistry". In order to enhance the wanted interactions and reduce the unwanted ones, good knowledge in process water chemistry is desirable.

# The aim of the work

The main objective of the work was to clarify important parameters that affect the adsorption of colloidal wood resin by small particles like fillers or fines. Special attention has been given to the effect of dissolved substances and the effect of different types of fines in mechanical pulp. The characteristics and behaviour of fines, among others the bulk and the surface composition and the origin of charged groups, were investigated in detail. The possibilities of targeted fixation, *i.e.* making certain surfaces adsorb the colloidal wood resin, were determined using cationic and neutral polymers.

Such specific adsorption or targeted fixation of colloidal wood resin to surfaces is in many situations considered desirable. In order to minimize the strength-reducing effect of the wood resin in paper, adsorption or fixation of the colloidal wood resin to low bonding surfaces in the process water is an obvious strategy. Examples of such low bonding surfaces are fillers and flake-like fines.

# Background

In addition to suspended fibres, the main components in the process water used with a paper machine making wood containing paper are dissolved and colloidal substances (DCS), particles like fillers and fines and additives like polymers to enhance retention and fixation. The fines and the DCS originate from the wood chips, while the fillers and fixation and retention aids are added to the process.

Table 1. Typical amounts of dissolved and colloidal substances in 1% suspension of unbleached spruce TMP (Holmborn 1997)

| Wood component                                   | Amount (kg/t TMP) |
|--|-------------------|
| Acetic acid                                      | 1 - 2             |
| Lignans  | 2 - 3             |
| Wood resin                                       | 4 - 6             |
| Hemicelluloses and pectin                        | 18 - 21           |
| Lignin and lignin-like oligomers                 | 3-5               |
| Other components: colloidal fines, proteins etc. | 6 - 8             |

The following gives a comprehensive description the main groups of components, and some important aspects of how they behave in process water.

#### **Dissolved material**

The dissolved material released from mechanical pulp is composed of a wide range of different compounds. Some of the released material is inorganic, like *e.g.* salts, but the majority of the compounds is organic. This organic material consists of hemicelluloses, pectin, lignans, lignin and lignin-like oligomers and acetic acid (Holmbom 1997). In actual mill practice, the amount and composition of the dissolved material is dependent on many factors, such as the quality of wood furnish, pulping process conditions, the water configuration of the mill and the degree of water closure.

Hemicelluloses make up a major part of the dissolved substances (Table 1), and *O*-acetyl-galactoglucomannan is the main dissolved hemicellulose (Thornton *et al.* 1994a). Dissolved *O*-acetyl-galactoglucomannan does not contain carboxylic groups, and is composed of mannose (Man), glucose (Glc) and galactose (Gal) with a Man:Glc:Gal ratio of approximately 4:1:0.6 (Thornton *et al.* 1994a). At pH levels above 8, *e.g.* in peroxide bleaching, the *O*-acetyl-galactoglucomannan is deacetylated. Without the acetyl side group, the galactoglucomannan can adsorb onto fibres in TMP suspensions (Thornton *et al.* 1994b). Mainly deacetylated, but also acetylated galactoglucomannans adsorb to bleached kraft fibres (Hannuksela and Holmbom 2001) which is often added to the mechanical pulps in order to enhance the paper strength.

The two hemicelluloses arabino-4-O-methylglucuronoxylan (Thornton *et al.* 1994a) and arabinogalactan (Willför *et al.* 1999) are also to some extent dissolved, but the amounts are small compared to O-acetyl-galactoglucomannan. The two polysaccharides both contain some carboxylic acid groups with pK<sub>a</sub> values between 3 and 4. Since the pH of

the mechanical pulping process water is normally around 5, these acid groups are charged and thus contribute to the cationic demand.

Pectin consists mainly of partly methylated galacturonic acids and is found in the primary wall, middle lamella cell corners, ray cells and in the tori of the bordered pits (Westermark and Vennigerholtz 1995). Some of the pectin may be dissolved into the water phase, particularly under alkaline conditions (Thornton *et al.* 1994a). These potentially highly charged polymers can give a significant contribution to the amount of charged groups in the pulp and process water (Sundberg *et al.* 2000a). Such charged groups are known to consume cationic polymers like retention- and fixation aids in the process water and thus reduce the effect of the added polymers.

Lignin and lignans are also dissolved from mechanical pulp. Both groups adsorb ultraviolet light at 280 nm (UV280) and are often denoted "lignin-like material". The lignans are readily released into process water (Jørgensen *et al.* 1995), and consist of two phenylpropane units bound together at their  $\beta$ -carbon. The dissolved lignin is structurally similar to lignin found in wood, but has a low molecular weight. In the process water they do not interact with cationic polymers, but they may contribute to the darkening of the water and the decrease in the brightness of paper made in highly closed systems.

The dissolved material was earlier measured as the chemical oxygen demand (COD) or total organic carbon (TOC). These methods are still used but advances in analytical chemistry have resulted in methods which give more precise information about the amount and composition of the dissolved material. The amount and composition of dissolved carbohydrates are now usually measured on a gas chromatograph after the carbohydrate oligomers or polymers are broken down to monomers. This depolymerisation can be done with sulphuric acid, in which all the polysaccharides are broken down to monomers. The separation in a gas chromatograph (GC) may be done for the monomers. The two main disadvantages with the sulphuric acid depolymerization method are that it decomposes some of the monomers, like uronic acids, and that the hydrolysis yield may vary between different polysaccharides. Using a more careful de-polymerization, like the methanolysis, it is possible to measure the uronic acids (Sundberg et al. 1996c). This de-polymerization method cannot be used to measure the amount of cellulose since it is only slightly decomposed. The lignin-like components in the process water are often determined by measuring the absorbance at 280 nm. Both lignin and lignans are measured in this way, but by extracting the lignans from the process water with methyl *tert*-butyl ether (MTBE) (Örså and Holbom 1994) the residual lignin may be determined.

#### Wood resin

Wood resin consists mainly of the hydrophobic compounds fatty acids, resin acids, triglycerides, sterylesters and sterols. This material is extractable with organic solvents like acetone or dichloromethane (DCM), and constitutes 1 - 2% of Norway spruce (*Picea abies*) wood. Some of this wood resin is liberated from the wood matrix and transferred to the water phase, particularly in the early stages of the pulping process.

Käyhkö (2002) measured that 49% of the wood resin had been transferred to the water phase already in the pulper after the refiner. After the latency chest an additional 8% of the wood resin was dissolved or dispersed in the water phase. The extent to which wood resin, or hydrophobic extractives, is transferred to or from the water phase at later process stages is dependent on many process conditions. Käyhkö (2002) pointed out important process parameters like the pH level, whether the pulp was peroxide bleached or not, the mixing time and intensity, the use of dispersing agents and the content of electrolytes.

Due to its low solubility in the process water, the hydrophobic wood resin is mainly attached to particles (Magnus et al. 2000a) or exists as suspended colloids in the sizerange of 0.1-1 µm (Nylund et al. 1993; Swerin et al. 1993). In pure dispersions the colloidal wood resin, or extractives, are electrostatically stabilised and may thus be destabilised by the addition of simple electrolytes (Sundberg et al. 1996a). An increased amount of fatty acids, and also to some extent resin acids, will increase the surface charge density of the colloidal wood resin resulting in increased stability of the colloidal droplets (Sihvonen et al. 1998). The carboxylic acids groups on the hydrophobic molecules are probably oriented towards the surface of the colloidal droplets (Nylund 1997) contributing to the surface charge at pH values above the  $pK_a$  of the acid groups. The charge density on the surface of the colloidal droplets is thus dependent on the pK<sub>a</sub> of the carboxylic acids, correcting for the apparent dissociation constant (Laine et al. 1994a), and the pH of the surrounding solution. The apparent dissociation constant is different from the real dissociation constant because the concentration of hydronium ions increases close to a charged surface while the pH is measured in the bulk solution with a lower concentration of hydronium ions.

However, in the process water in pulp and paper plants the colloidal wood resin is quite stable against electrolyte-induced aggregation. In such process water the colloidal wood resin has additional stability caused by the dissolved components (Sundberg *et al.* 1996b). Different polysaccharides, but especially galactoglucomannan, participate in the steric stabilisation (Sundberg *et al.* 1996b). It has also been suggested that other dissolved components like water soluble lignosaccharides (Koshijima *et al.* 1989; Jacobs 1995) or proteins (Sundberg 1995) contribute to the steric stabilisation. This steric stabilisation of the colloidal extractives is strongest in water separated from unbleached TMP, where agglomeration caused by the addition of simple electrolytes is minor (Sundberg *et al.* 1994b). In order to aggregate the sterically stabilised colloidal extractives in mechanical pulp process water effectively, organic or inorganic fixation agents are often needed (Sundberg *et al.* 1994a; Paper VII).



Figure 1: Illustration of electrostatic and steric stabilisation of colloidal wood resin

Peroxide bleaching of mechanical pulp results in destabilisation of the colloidal wood resin (Sundberg *et al.* 1994b). Since the peroxide does not penetrate the resin aggregates (Holmbom 2000), the changes that cause this destabilisation are mainly a result of reactions with dissolved components. Sundberg (1995), for example, has demonstrated that the deacetylation of dissolved galactoglucomannan causes the polysaccharide to adsorb to fibres and reduces the steric stabilisation of the colloidal wood resin.

Colloidal wood resin which is destabilised is more easily adsorbed to surfaces (Holmbom *et al.* 1995). Wood resin adsorbed to surfaces of fibres or fines may change the property of the resulting paper. The strength reducing effect of the wood resin on paper has been long known (Brandal and Lindheim 1966) and is explained by the ability of the wood resin to prevent bonding between fibres or fines. The reduced amount of bonds between fibres or fines also changes other properties of the paper and the results include lower density and increased light scattering (Sundberg *et al.* 2000b). When dissolved substances like polysaccharides are retained in the paper sheet together with the wood resin, the detrimental effect on paper strength is reduced (Sundberg *et al.* 2000b; Rundlöf *et al.* 2002). The mechanism is not clear, but a plausible explanation is that the dissolved substances screen the colloidal extractives in the sheet and thus reduce the detrimental effect of the strength.

An extraction step is needed in order to measure the amount of wood resin suspended in water. Extraction techniques like solvent-solvent extraction have been used frequently with organic solvents like diethyl ether (Alvarado *et al.* 1992) or methyl-*tert*-butyl ether (MTBE) (Örså and Holmbom 1994). The pH during extraction with MTBE has a large effect on the extraction efficiency particularly in process water from kraft pulp and paper mills (Voss and Rapsomatiotis 1985), but also from TMP process water (Hoel *et al.* 1996). At low pH levels dissolved lignin may precipitate, resulting in a co-precipitation of dissolved or colloidal substances that may influence the extraction efficiency. The solvent extraction techniques that are available are labour-intensive and consume large amounts of solvent. As a result, attempts have been made to find more

rapid and easy methods for extraction of the colloidal wood resin using, for example, solid phase extraction (SPE) (Paper I).

#### Definition and properties of fines

Fines may be viewed as fibre fragments and are thus much smaller than fibres. A widely used definition of fines is the fraction of a pulp suspension that passes a 200 mesh screen ("P200 fraction") during standardised conditions in a Bauer McNett fractionation apparatus. This definition gives an approximate upper level for the size of the fines, but not a lower one. The boundary between fines and DCS is unclear, but fines may be interpreted as the particles that are visible in a light microscope (Luukko 1998). Generally there is an unclear boundary between "microscopic" and "colloidal" size ranges.

Fines in mechanical pulps consist of a number of different types of particles. Rundlöf (2002) has summarised the different types of fines as mainly flake-like pieces from the middle lamella, and band- and thread-like particles from the secondary wall (fibrillar fines). These fines are produced during the extensive mechanical treatment in the refining process, and are peeled off mainly from the outer parts of the fibre. There are also ray cells and fragments with more or less intact pores, as well as colloidal fines ("microfines"). Only the large fraction of the microfines can be separated from dissolved and colloidal substances by ultra-centrifugation (Nylund *et al.* 1994).



Figure 2: Fines in TMP (Rundlöf 2002).

With low total specific energy consumption (SEC) mainly flake-like fines will be produced. Whereas, with high total SEC, flake-like fines are produced in the early refining stages and fibrillar fines the later stages (Luukko and Nurminen 1999). Heikkurinen and Hattula (1993) used this knowledge to produce different kinds of fines by successive refining. The fines they produced in the first refining had a shorter average length, lower specific sedimentation volume and higher lignin content than the fines produced in later refining stages.

The properties of fines are very often described as their effect on the quality of paper. Paper made from mechanical pulps will normally contain 10-30% fines and the presence of fines in the paper has been found to have a strong influence on paper properties like tensile index, tear index, roughness, light scattering and density (Mohlin 1980; Retulainen *et al.* 1993; Moss and Retulainen 1995). The various types of fines have different effects on the paper. In general, paper containing fibrillar fines are denser, have a higher tensile index and a lower light scattering coefficient than paper containing flake-like fines (Heikkurinen and Hattula 1993: Luukko and Paulapuro 1999a). The effect of the fibrillar fines on sheet properties has been shown to resemble the effect of bleached kraft fibrils (Luukko and Paulapuro 1999a).

In order to explain the properties of fines and the effect of fines on paper properties, both physical parameters such as size and shape (Forgacs 1963; Luukko and Paulapuro 1999a) and chemical parameters like the lignin and carbohydrate composition (Heikkurinen and Hattula 1993; Luukko *et al.* 1999) have been used. Physico-chemical properties such as the amount of charged groups may also be important. The stiff flake-like fines, which have the highest content of lignin, show the poorest bonding ability (Luukko *et al.* 1999). The high content of lignin may reduce the ability of the fines to create inter-particle hydrogen bonds and reduce the flexibility. These two effects may reduce the bonding area and strength, and thus create a weaker and less dense sheet. In contrast, the fibrillar fines are thread- or band-like, and contain more carbohydrates which can create inter-particle hydrogen bonds. Both the shape and the chemical composition may increase the flexibility and the bonding ability of the particles resulting in a denser and stronger paper sheet.

#### Fines in process water

The quality of fines circulating in the process water is known to deteriorate, a process which sometimes is termed "aging of fines". The circulating fines are darker and they give a lower contribution to the strength properties of the paper than fresh fines. There may be several reasons for the deterioration of the circulating fines including adsorption of contaminants or enrichment of particular types of fines. The darkening of the fines, which of course can be counteracted by increased use of expensive bleaching chemicals, is caused by a combination of the adsorption of coloured substances and the creation of chromophores (Rundlöf et al. 2000c). The adsorption of acetone-extractable compounds in the process water is one important reason for the lower contribution to the strength properties of the paper (Rundlöf et al. 2000c). When colloidal wood resin is adsorbed to fines, which is often done with the aid of cationic polymers in paper mill process water, a similar detrimental effect on the quality of the fines has been observed (Rundlöf et al. 2000b). Rundlöf et al. (2000c) reported that the detrimental effect of extractives adsorbed to fines correlated well with the measured amount of extractives on the surface, but in the work by Luukko and Paulapuro (1999b) this relationship was not equally clear. It is unclear whether this adsorption is reversible. However, a large part of the dichloromethane (DCM) extractable compounds can be removed by washing with large quantities of water (Rundlöf et al. 2000a). Paper containing fines that are separated in a Bauer McNett fractionator has been found to be stronger and have less light absorption compared to paper containing fines separated in a Britt Dynamic Drainage Jar (BDDJ) (Rundlöf *et al.* 2000a). A major difference between the two methods is the large amounts of water used in the Bauer McNett fractionator compared to the BDDJ, resulting in washed fines.

It is unclear which factors influence the adsorption of the acetone-extractable compounds to fines, but the stability of the colloidal wood resin, the surface area and the surface properties of the fines are probably important. This is further investigated in Paper III. Due to the lack of good analytical tools, the surface area and the surface properties of the fines are particularly difficult to measure. The specific surface of fines is clearly much larger than mechanical pulp fibres, which has been reported to be in the range  $1.38 - 2.63 \text{ m}^2/\text{g}$  (Johansson 1998). Wood and Karnis (1996) used turbidity measurements and the water content of the fines (as fibre saturation point) to calculate the specific surface of groundwood pulp fines and they found it to be about  $13 \text{ m}^2/\text{g}$ . The fines thus have a specific surface in the range of ten times larger than fibres which make them suitable for potentially adsorbing large amounts of contaminants in the process water.

#### **Swelling of fines**

Another property the fines posses when they are suspended in process water is their ability to swell. The swelling of fines, or pulp, may be viewed as its ability to hold water and is thus expected to strongly influence the ability of the paper machine to run well. Increased swelling of the pulp will either increase the dewatering rate of the pulp resulting in a slower paper machine, or increase the energy demand in the drying section of the paper machine. In addition to the effects on the paper machine, the swelling of pulps also has a strong influence on the quality of the paper. Paper made of chemical pulps is known to increase in strength as the fibres become more swollen (Lindström 1992, Laine and Stenius 1997). Paper made of chemimechanical pulp may also be affected in a similar way. This was demonstrated by Zhang et al. (1994) who found that with an increasing content of charged groups, which probably causes more swollen pulp, the tensile index of the paper sheets rose. Swelling is often measured as the content of water in the fibres, either as water retention value (WRV) or fibre saturation point (Stone and Scallan 1968). Also other more recent techniques are available like differential scanning calorimetry (Maloney and Paulapuro 1999) and NMR (Blicharska and Kluza 1996).

The degree of swelling is determined by the balance between the osmotic pressure and the elastic restraining force (Flory 1953). If the change in chemical potential of the water inside the fines due to the mixing of water with solvated macromolecular segments is  $\Delta \mu_{osm}$  and the change in chemical potential of the water due to the elastic reaction of the fines is  $\Delta \mu_{el}$ , then, at equilibrium (Smidsrød and Moe 1995)

#### $\Delta \mu_{\rm osm} + \Delta \mu_{\rm el} = 0 \qquad \qquad Equation \ 1$

Of the wood polymers, lignin swells less than the carbohydrates (Lindström and Westman 1980; Westman and Lindström 1981). Especially below the softening temperature, the stiff lignin will increase the elastic restraining force and counteract the swelling of fibres (Eriksson *et al.* 1991). Flake-like fines that contain a higher amount of

lignin (Sundberg *et al.* 2001) have thus been shown to swell less than the fibrillar fines (Luukko and Maloney 1999). In addition to the amount of lignin versus carbohydrates, the amount of charged groups and counter-ions also greatly influences the swelling of fibres (Lindström 1992: Scallan and Tigerström 1992). The charged groups will increase the osmotic pressure, especially at low ionic strengths, and thus contribute to a more swollen fibre. The  $\Delta \mu_{osm}$  is thus the sum of the change in the chemical potential of the water due to soluble material inside the fines,  $\Delta \mu_p$ , and the change in chemical potential of the outside of the fines,  $\Delta \mu_i$ 

$$\Delta \mu_{\rm p} + \Delta \mu_{\rm i} + \Delta \mu_{\rm el} = 0 \qquad \qquad Equation \ 2$$

The charged groups in wood, and thus in fines, originate from acidic groups (Sjöström 1989). At a pH significantly lower than the pK<sub>a</sub> for these acids, there are minor charges in the fines and  $\Delta \mu_i \approx 0$ . Some of the hemicelluloses like xylan, and other polysaccharides like pectin, contain such chargeable groups (Fengel and Wegener 1989; Sundberg *et al.* 1998). Pectin, which is a highly charged polysaccharide under normal papermaking conditions (Sundberg *et al.* 1998), is found in the middle lamella and the tori of the bordered-pit membranes (Westermark and Vennigerholtz 1995). Flake-like fines, which originate from these pectin rich areas, are thus expected to contain a higher amount of pectin and possibly more charged groups than the fibrillar fines. The amount and origin of the charged groups in fines are investigated in Paper II. The pectin in the fines can be demetylated by either alkali treatment or peroxide bleaching which will increase the number of charged groups. Such treatments may also change the lignin. Alkali treatment or peroxide bleaching will thus probably increase the swelling of the fines, but this is further investigated in Paper III.

#### Fillers in process water

The collective term "fillers" is used for a number of different components that are mainly inorganic. Examples of such components are calcium carbonate (CaCO<sub>3</sub>), talc, kaolin and different silicates. Fillers are often introduced to the papermaking process to increase the opacity of the finished paper or to reduce the consumption of more expensive pulp. In newspaper grades the filler content is often between 0 and 10%, while magazine paper may have a filler content of up to 30%.

Fillers, like the fines, are small and thus have a large specific surface. Typical surface areas of the fillers are between 5 and 10  $m^2/g$  (Eklund and Linström 1991) which can adsorb large amounts of contaminants. In pure water suspensions, without any dissolved material present, minerals like talc, kaolinite and montmorillonite readily adsorb oleic acid in a way that correlates well with the Langmuir model (Rogan 1994). Rogan (1994) also showed that triolein, a triglyceride, may adsorb to different minerals, particularly to hydrophobic surfaces like talc.

It is possible to estimate if the adsorption of colloidal wood resin to different fillers in water is possible by using the theory developed mainly by Good and Van Oss (see for

example Van Oss 1994). This may be done by using Equations 3 to 11, as described below.

The work of adhesion between wood resin and water  $(Wa_{rw})$  is given by

$$Wa_{rw} = \gamma_r + \gamma_w - \gamma_{rw} = \gamma_w (1 + \cos\theta)$$
 Equation 3

where  $\gamma_w$  is the surface tension of water,  $\gamma_r$  is the surface energy of wood resin,  $\gamma_{rw}$  is the interfacial energy wood resin and water, and  $\theta$  is the contact angle between water and wood resin. The free energy of interaction (Van Oss 1994) at contact between wood resin and a filler surface immersed in water is given by

$$\Delta G_{fwr} / A = \gamma_{fr} - \gamma_{fw} - \gamma_{rw} \qquad Equation 4$$

and the free energy of interaction at contact between wood resin immersed in water is given by

$$\Delta G_{rwr} / A = -2\gamma_{rw} \qquad Equation 5$$

where  $\gamma_{fr}$ ,  $\gamma_{fw}$  and  $\gamma_{rw}$  are the interfacial surface energies between filler and wood resin, filler and water, and wood resin and water respectively. A is the surface area of contact. In this context contact means a distance between the particles of 0.157 nm (Van Oss 1993). Equations 4 and 5 do not give any information about whether adsorption or agglomeration actually occurs. Calculation of the latter involves a full energy plot with distance, which is mainly covered by the DLVO theory up to small distances. Such plots often give an energy barrier between two closing particles, resulting in kinetically stabilised dispersion. But the sign and magnitude of  $\Delta G_{fwr}$ , as a first approximation, can give an indication whether the adsorption is possible or not. The terms included are assumed to reflect the actual situation, neglecting the electrostatic interaction. If, for example,  $\Delta G_{fwr}$  from Equation 4 is negative, the adsorption of colloidal wood resin in water to fillers is energetically favourable, given that the Lifshitz-van der Waals and the Lewis acid-base interactions are the main contributors to the interfacial interactions. Adsorbed polymers on the surface of the colloidal wood resin or filler resulting in steric stabilisation would of course alter the situation. The interfacial surface energy may be calculated using Equations 6 to 8 (Van Oss et al. 1988)

$$\gamma_{fr} = \gamma_f + \gamma_r - 2 \cdot \left(\sqrt{\gamma_f^{LW} \cdot \gamma_r^{LW}} + \sqrt{\gamma_f^+ \cdot \gamma_r^-} + \sqrt{\gamma_f^- \cdot \gamma_r^+}\right) \qquad Equation \ 6$$

$$\gamma_{fw} = \gamma_f + \gamma_w - 2 \cdot \left(\sqrt{\gamma_f^{LW} \cdot \gamma_w^{LW}} + \sqrt{\gamma_f^+ \cdot \gamma_w^-} + \sqrt{\gamma_f^- \cdot \gamma_w^+}\right) \qquad Equation \ 7$$

$$\gamma_{rw} = \gamma_r + \gamma_w - 2 \cdot (\sqrt{\gamma_r^{LW}} \cdot \gamma_w^{LW} + \sqrt{\gamma_r^+} \cdot \gamma_w^- + \sqrt{\gamma_r^-} \cdot \gamma_w^+) \qquad Equation \ 8$$

where  $\gamma_{fi}$   $\gamma_r$  and  $\gamma_w$  are the surface energy of the filler, wood resin and the surface tension of water, respectively. The superscript LW refers to the Lifshitz-van der Waals contribution, and the superscripts + and – refer to the acid and base contributions to the surface tension or energy. In order to determine the three contributions, Equation 9 may be used (van Oss *et al.* 1988)

$$(1 + \cos\theta) \cdot \gamma_L = 2 \cdot (\sqrt{\gamma^{LW}} \cdot \gamma_L^{LW} + \sqrt{\gamma^+} \cdot \gamma_L^- + \sqrt{\gamma^-} \cdot \gamma_L^+) \qquad Equation 9$$

where  $\gamma^{LW}$ ,  $\gamma^+$  and  $\gamma^-$  are the Lifshitz-van der Waals contribution, the acid contribution and the base contribution to the surface energy of filler or wood resin.  $\theta$  is the contact angle between a liquid and the solid surface, denoted with subscript L. The relation between the surface tension or energy and the contribution components is

$$\gamma_{1} = \gamma_{1}^{LW} + \gamma_{1}^{AB} = \gamma_{1}^{LW} + 2 \cdot \sqrt{\gamma_{1}^{+} \cdot \gamma_{1}^{-}}$$
 Equation 10

where the superscript *AB* refers to the acid-base contribution. The set of equations (Equations 4-10) allows us to calculate the free energy of interaction between two particles immersed in water (Equations 4 or 5) if we know the contributions to the surface energy of the components (Equations 6-8). These contributions may either be found in the literature or measured (Equations 3 and 9). The different contributions to the total surface tension or energy are related by Equation 10. Positive free energy values indicate repulsion between the particles, and a negative value indicates attraction. It is important to bear in mind that the validity of this theory, which was developed mainly by van Oss and Good, is debated. The assumption that the surface energy of a material can be split in several components has been especially criticised (Kwok 1999).

When the fillers are introduced into more complex suspensions, like process water containing dissolved wood polymers, the adsorption of colloidal wood resin is probably dependent on the degree of steric stabilisation. Peroxide bleaching is known to change the properties of the dissolved material (Holmbom 1997) causing reduced stability of the colloidal wood resin. Such treatment can thus increase the tendency of the colloidal droplets to adsorb to fillers which has been observed by Willför *et al.* (2000). The effect of dissolved material on the adsorption of colloidal wood resin to fillers is more closely investigated in Paper VI. Also other hydrophobic contaminants like wax, toner ink, hot melt and adhesives, which can cause problems in mills using recycled pulp, have the potential to become adsorbed by fillers (Yordan *et al.* 2001).

#### Retention aids and fixatives in process water

In papermaking, polymers are often added to the process in order to increase the retention of small particles like fillers and fines (retention aids) or to adsorb, or fix, dissolved and colloidal substances (DCS) to the fibre web (fixatives). Such additives are also known as process aids since they are used to improve the production efficiency.

Polymers used for the fixation of DCS are often highly charged with a low-molecular weight, and follow a charge neutralisation mechanism (Wågberg and Ödberg 1991). Small and high-charged cationic polymers may also adsorb to a negatively charged surface and create a local positively charge area ("patch"). This "patch" may interact with negatively charged surfaces on other particles, resulting in flocculation and improved retention. Large and low-charged polymers may adsorb to a particle while

part of the polymer still is in the surrounding solution. These loops or tails may adsorb to other particles, creating a bridge, and the result is large flocs which are retained in the fibre web.



Figure 3: Illustration of the bridging (above) and the patch (below) mechanisms

Independent of the fixation or retention mechanism, the polymers must adsorb to the surface of the particles. The driving force of this adsorption can be quantified by the parameter  $\chi_s$ , which is the adsorption enthalpy per segment. This parameter has different contributions (as summarised by Van de Ven 2000)

$$\chi_s = \chi_s^0 + \chi_s^{el} \qquad Equation 11$$

where  $\chi_s^0$  and  $\chi_s^{el}$  is the non-electrostatic and the electrostatic contribution. In the case of non-charged polymers, like polyethyleneoxide (PEO), only  $\chi_s^0$  contributes to the adsorption enthalpy per segment. Cationic polymers are known to readily adsorb to surfaces with anionic charged groups, like fibres and colloidal wood resin (Wågberg and Ödberg 1991; Wågberg and Kolar 1996; Nurmi and Eklund 2000). Many of these cationic polymers adsorb to the anionic sites by an 1:1 ion-exchange mechanism (Wågberg *et al.* 1985) where the entropy gain of the released counter-ions gives a large contribution to the adsorption energy (Wågberg 2000; Van de Ven 2000). This explains why the cationic polymers often show a reduced efficiency when the salt concentration in the process water increases as a result of reduced fresh water consumption. Polymers with a higher charge density are often introduced to counteract this reduced efficiency.

The uncharged polyethyleneoxide (PEO) has to some extent been used as a retention aid during papermaking, especially in mechanical pulp furnishes. An advantage with the PEO is that the polymer does not interact with anionic sites in the DCS fraction. PEO has an affinity towards phenolic groups (Scott 1996), and probably only adsorbs to the external surface of fibres (Van de Ven 2000). Fibres that contain few phenolic groups, like bleached kraft fibres (Laine *et al.* 1996) do not adsorb PEO (Picaro and Van de Ven

1995; Van de Ven and Alince 1996). The polymer may be used alone or, more frequently, together with a cofactor. Such cofactors contain phenolic groups, and interact with PEO in such a way that the retention efficiency is increased. The retention mechanism in which PEO/cofactor works was earlier suggested to be a network flocculation, but now polymer bridging is more accepted (Van de Ven and Alince 1996). Carignan *et al.* (1998) suggested that without cofactor PEO might adsorb to some fines but not to others, leading to asymmetric polymer bridging. Such specific adsorption may be useful since it makes "targeted adsorption" possible. Whether colloidal wood resin more easily adsorbs to certain fines with the aid of PEO is investigated in Paper V.

# Materials and methods

#### Production and isolation of different fines

Norway spruce wood chips (~98% *Picea abies*) were sampled from a Norwegian integrated newsprint mill. After steaming at 100°C for 15 minutes, the wood chips were refined in an atmospheric 20" pilot scale refiner. The refined pulp was diluted to 1% consistency with hot water and mixed in a pulper for minimum 15 minutes. Then the suspension was dewatered by a screw press. The pulp was diluted and dewatered 2-7 times until the water was clear, judged visually, indicating that the fines had been removed from the pulp. The residual fines content in the washed pulp was determined with a Bauer McNett fractionator to be between 0 and 6% depending on the refining stage. After washing, the pulp was refined again. In this way the pulp was refined 4 times successively. The specific energy consumption (SEC) of each refining stage was between 450 and 885 kWh/tonne. The fines produced in the first, third and fourth refining stages were collected.

The diluted fines suspension from the screw press was filtered through a 76  $\mu$ m (200 mesh) Attisholtz-filter in order to separate fibres and fines. The fines were allowed to settle for one day before the supernatant was pumped off. In order to reduce the amount of extractives associated to the fines, the fines were washed further by diluting water to a consistency of 0.1%. The fines were allowed to settle before the supernatant was removed. More water was removed by centrifugation to a dry content of 10 - 20% before the fines were stored in a freezer at  $-18^{\circ}$ C.

#### **Chemical analysis**

The amount of pectin and hemicellulose in the fines or in solution was measured according to a method described by Sundberg *et al.* (1996c). The total carbohydrate composition was measured using the standard TAPPI method (T 249 cm-85) with the modifications described by Cao *et al.* (1997), while the total amount of hexose carbohydrates in solution was determined spectrophotometrically using the sulphuric acid method (Dubois *et al.* 1956; Chaplin and Kennedy 1986). The amount of reducing sugars was determined according to a method by Nelson (1944) and assumed equal to the number of carbohydrates.

The amount of lignin in the fines was determined as acid insoluble and acid soluble lignin according to the method described by Dence (1992).

The amount of polyethyleneoxide in solution was determined, after correcting for the background, according to Attia and Rubio (1975).

The number of charged groups, as well as surface charge, was measured by polyelectrolytic titration (Wågberg *et al.* 1989). Two different polymers, polybrene and poly-DADMAC, were applied (Allied Colloids) and used without further purification.

Extractives in suspension were extracted with methyl *tert*-butyl ether (MTBE) (Holmbom and Örså 1993, Magnus *et al.* 2000b) and analysed by GC-FID (Ekman and Holmbom 1989) in order to measure the amount of the individual extractive components.

#### Surface characterization of fines

The surface composition of the fines or paper was measured by ESCA (Electron Spectroscopy for Chemical Analysis) and the surface composition was calculated according to Luukko *et al.* (1999). The contact angles were measured with a dynamic adsorption tester (DAT 1100 from Fibro Systems AB, Sweden) (Tappi T 558 om-97). In order to measure the contact angles between extractives and different liquids a plastic coated paper was covered with extractives prior to the contact angle measurements. This coverage was done by placing an acetone solution with extractives on the surface of a plastic coated paper and letting the acetone evaporate. This was repeated several times until the extractive layer was clearly visible to the eye.

#### **Physical testing of fines**

The fibrillar and ray cell content (mass proportion, %) of the fines fractions was done according to Luukko *et al.* (1997).

Turbidity has been reported to be a convenient method to determine the specific surface of fines (Wood and Karnis 1996). Samples with fines were repeatedly washed in order to eliminate the contribution from the colloidal material to the turbidity. The separation of fines and colloidal material was done with a centrifuge (500g, 30 min). The turbidity of the fines that was free from colloidal material was then measured at different concentrations.

The cross-sectional fibre dimensions were measured by digitalised scanning electron microscope (SEM) images by the method described by Reme and Helle (1999) using the Bauer McNett +50 mesh fibre fraction. Both the mean wall thickness and the variance of the wall thickness around the perimeter were calculated. The reported values are average values for measurements of at least 750 fibres.

#### Preparation of model colloidal extractives and model dissolved substances

Preparation of model colloidal wood resin was done according to Sundberg *et al.* (1996a). This resulted in a model colloidal dispersion with a particle diameter from 0.1 to 2  $\mu$ m (Paper IV). The acetone was removed by dialysis against water, using a Spectra/Por 4 dialysis membrane with a molecular cut-off of 12-14000 (according to the supplier). The dialysis tube was placed in a bucket and tap water was added continuously for a minimum of two days. In the last 6 hours purified water was applied. The model solutions of dissolved substances was prepared as described in (Paper IV) which is based on the procedure by Sundberg *et al.* (1996b). The filtered solution was dialysed for a minimum of two days, using a Spectra/Por 4 dialysis membrane, resulting in a solution with less turbidity than 5 nephelometric turbidity units (NTU).



Figure 4: Preparation of model colloidal extractives and model dissolved substances

#### Solid phase extraction (SPE)

Model white water was produced in the laboratory (Örså and Holmbom 1994; Thornton *et al.* 1991). Acetone was added to the model white water and filtered (GF/A). The filters and the sample bottles were washed with acetone and water (5 mL, 1:1) which was added to the filtered samples and applied to the column. The solid phase extraction (SPE) was executed on a solvated C18 (EC) column, and the extract was eluted with methanol and dichloromethane before dying and further analysis involving a gas chromatograph (GC).

#### Swelling

The fibre saturation point (FSP) was measured according to Luukko and Maloney (1999), based on the method developed by Stone and Scallan (1968). A dextran polymer (T2000 from Pharmacia) was used in the measurements ( $Mw = 2x10^6$  g/mole).

Prior to the measurement the fines were treated with 0.1 M HCl for 15 minutes. Next, the fines were washed until the washing water had conductivity  $<10 \ \mu$ S/cm. Finally the fines were suspended in a solution containing ion exchanged water (18.4 M $\Omega$ ) and either HCl at pH 2 (ionic strength (I) = 0.01M) or buffer (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa) at pH 5.4 (I = 0.01M). This resulted in either H-form or Na-form of the acids groups in the fines.

#### Alkali treatment and peroxide bleaching

Suspensions were alkali treated by adding NaOH until pH 11.2-11.5. The suspensions were exposed to this high pH for 90 minutes at 60°C, before acidifying to about pH 6.0 with HCl.

Peroxide bleaching of the fines was done by first adding 0.02 g DTPA/10 g fines. After one hour in room temperature the fines were dewatered. Next, 0.3 g sodium silicate and

1.143 g peroxide were added per 10 g fines. Finally, NaOH was added until pH reached 11.2 - 11.5. The polyethylene bags with the fines (6.0 ± 0.2%) and the chemicals were mixed and placed in water baths at 60°C for 90 min. Adding HCl to pH 6 stopped the reaction.

#### Preparation and testing of laboratory sheets

Refiner mechanical pulp, washed free from fines, was disintegrated and mixed with the fines suspension giving a pulp with 30% fines and 70% fibres which was used to make laboratory sheets (SCAN-CM 64:00). The first 10 sheets produced were wasted in order to reach an assumed equilibrium between the composition of the added material and the composition of the laboratory sheets. The fibre and alkali treated fines were suspended in tap water, tap water with 64 g NaCl/L or tap water with a model colloidal dispersion ( $\approx 110$  mg extractives/L).

Tensile strength (SCAN-P 16:76), Z-strength (Tappi UM 403) and density were measured. The hydrophobic material in the laboratory sheets was measured after extraction with acetone (SCAN-CM 49:93).

#### **Adsorption measurements**

In adsorption measurements without polymers or dissolved substances (Paper VIII), the model colloidal extractives were simply added to the suspended fines. The pH and salt concentration was adjusted with HCl, NaOH or NaCl. The suspension was agitated slowly by a magnetic stirrer for 30 minutes at room temperature before the residual colloidal extractives was determined in the supernatant after centrifugation (500 g for 30 min).

In measurements with polymers or dissolved substances (Papers IV and V) the model colloidal extractives were first mixed with the dissolved substances. The solution was slowly agitated for one hour. Fines and the appropriate amount of buffer (at pH 2.2 or 5.4) were also mixed and agitated slowly for one hour. The buffers had an ionic strength of 5-10 mM. The two solutions were then mixed and slowly agitated. In the trials where polymers were added, this was done at this point. After an appropriate amount of time (15 min in the polymer trials where constant time was used, two hours if no polymer was used) the suspension was centrifuged (500 g for 30 min) to separate the particles from the model colloidal extractives. The turbidity or the absorbance at 450 nm of the supernatant was then measured and taken as the amount of model colloidal extractives not adsorbed to the particles.

In the adsorption measurements of model colloidal extractives to fillers (Paper VI), the fillers were washed until the wastewater had conductivity  $<20 \ \mu$ S/cm. The fillers were then suspended in buffer (pH 5.4 and I=0.01M) to a concentration of 10 g/L and used without further purification. The addition of dissolved substances and model colloidal extractives were done as described above. The fillers used were kaolin, talc and magnesium-aluminium-silicate (Mg-Al-silicate).

The adsorption of polymers to the fines was measured as the difference in concentration before and after adsorption. The fines were removed by centrifugation, and the supernatant was analysed.

In Paper V the adsorption of dissolved components and PEO to extractive surface was measured using a quartz crystal microbalance and dissipation (QCM-D) apparatus (Rodahl *et al.* 1995).

# **Results and discussion**

The results and discussion chapter is divided into six parts. The first part describes the attempt to develop a faster method to measure the amount of extractives in water. This was done in order to make the succeeding adsorption measurements easier (Paper I). The second part describes how the fines were made, and the results of the analysis of the fines. The main aim was to describe the fines and determine their properties. Some of the results in this second part have also been presented in Paper II. The third part describes how the swelling of the fines responded to alkali treatment and peroxide bleaching (Paper III). The swelling of fines which is important in papermaking since it influences the dewatering rate of the paper machine and probably the paper quality. Parts four and five describes the adsorption of colloidal wood resin to the different fines are described. The adsorption was measured in gradually more complex systems. The first measurements were done in simple systems containing only fines and colloidal wood resin (Paper VIII). Dissolved substances were then added to the system (Paper VI) before, finally, synthetic polymers were added (Paper V). The main motivation was to investigate the possibility of targeted adsorption or fixation. Targeted adsorption or fixation is wanted because, in principle, it makes it possible to remove detrimental substances from the process water with the paper with a minimal reduction in the strength qualities. This can be done if the strength-reducing colloidal wood resin is adsorbed to low-bonding particles, like flake-like fines. Filler is another example of particles that do not contribute to the strength of the paper, and part six describes the adsorption of colloidal wood resin to three different fillers.

## 1. Extraction of hydrophobic material from process water (Paper I)

The main aim of this paper was to develop a rapid and simple preparation procedure for three important groups of hydrophobic extractives in white water and compare it with the established liquid-liquid extraction method. A swift extraction method would make the later adsorption measurements easier.

The work focused on the quantification of the free fatty acids, resin acids and sterols. These components are important parts of the composition of the colloidal wood resin in process water from mechanical pulp and paper production plants.

The established methyl *tert*-butyl ether (MTBE) liquid-liquid extraction method (Örså and Holmbom 1994) was compared with the solid phase extraction (SPE) method (Figure 5). In conclusion, the yield of the three groups of extractives and the reproducibility is similar between the two methods. By using the SPE and the liquid-liquid extraction methods the total concentration of extractives was respectively  $17.1 \pm 0.8 \text{ mg/L}$  ( $\pm 4.8\%$ ) and  $15.3 \pm 2.3 \text{ mg/L}$  ( $\pm 15.1\%$ ).

The time needed to conduct the extraction was less for the SPE than the liquid-liquid extraction method, in addition to a lower solvent consumption. A disadvantage with the SPE method was that there was always the risk of plugging. Attempts were made to reduce the plugging and the addition of acetone had a positive effect, but the problem was never totally eliminated. The model water was also filtered through 76  $\mu$ m to

remove large particles, which otherwise might have caused severe plugging problems. Extractives on these particles were thus not included in the extracted material. In later work the established MTBE liquid-liquid extraction procedure was used.



Figure 5: Concentration of extractives in total (mg/L) obtained by solid phase extraction (SPE) and the liquid-liquid extraction method.

#### 2. The production and analysis of fines (Paper II and additional data)

The main aim of the refining trials and the succeeding analyses was to produce large quantities of different types of fines. It was important to determine the properties of the fines produced in the refining trials and compare the results with published data of fines found in other mechanical pulps. The properties of the fines were determined by chemical analyses, measuring the shape of the fines, physical testing of laboratory sheets containing the different fines and measurements of the number of charged groups. The refining trials produced 0.5 - 1 kg of fines which was enough to do the different measurements, and still have enough fines for the later swelling measurements and adsorption trials (Papers III, IV, V and VIII). Compared to other ways of isolating the fines material, the main advantage with the successive refining method was the possibility of isolating large quantities of different fines.

#### The production of fines

Fines were produced twice in two separate refining trials, and results from the analyses of the fines from the first refining trial are presented in Paper II. In general, all the trends between the different fines observed in the two refining trials were similar, although the levels could show some variation.

During the two refining trials the energy consumption was monitored. In Figure 6 the energy consumption during one of the refining trials is shown and the figure illustrates how the energy consumption could vary within the refining trials. Because of this, the separated fines were blended well before dewatering to ensure that samples analysed later on were representative. Fractionation of the isolated fines showed that 99% (w/w) of a fines sample was fines according to the Bauer McNett definition.



Figure 6: An example of the measurement of energy consumption during the refining.

After each refining stage the fibre wall thickness of fibres that had not been split was measured, and the results for both of the refining trials are shown in Figure 7. As expected, the average fibre wall thickness is somewhat reduced after each refining stage which indicates that the fines produced in each refining stage originated from different parts of the fibre wall. Unfortunately, it was estimated that only approximately 25% of the fines produced were actually collected. Thus, there are possibilities of discrimination of certain types of fines during the purification steps.



Figure 7: The specific energy consumption and the mean fibre wall thickness of fibres that had not been split after each refining stage. The bars indicate 95% confidence interval (N>750).

Storage of the fines was a problem. The fines could either be dewatered (10-25%) and frozen, which was done here, or the fines could be stored dispersed in water after the addition of conservatives. The effect of conservatives, which are often quite reactive, is unknown particularly for longer storage periods. An advantage with keeping the fines frozen was that the properties of the fines did not change during storage (which lasted

up to two years). The first approach was thus chosen despite the fact that the freezing the fines may have altered their properties somewhat.

#### The morphology of the fines

The different types of fines in mechanical pulps are known to have different shapes. Figures 8a and 8b show SEM images of fines produced in the first and the last refining stage, which later are termed "flake-like fines" and "second fibrillar fines" respectively. The fines produced in the third refining stage are later termed "first fibrillar fines".



Figure 8a and b: Images of the fines produced in the first refining trial. The image on the left (picture a) is fines produced in the first refining stage (flake-like fines), and the image on the right (picture b) is fines produced in the last refining stage (second fibrillar fines).

As indicated in Figures 8a and 8b the fibrillar fines are more abundant in the later refining stages than in the early ones, and one way to measure the content of fibrillar material is to use the method developed by Luukko *et al.* (1997). This method is based on image analysis where fibrillar fines are distinguished from other fines by the grey tone of the image. The amount of fibrillar fines in the different fines fractions from the present refining trials was measured in this way, and the results are shown in Figure 9. The figure shows that the content of fibrillar fines increases with later refining stages since the fibrillar material is produced by a peeling action after the lignin-rich middle lamella has been removed from the fibre surface (Karnis 1994). Heikkurinen and Hattula (1993) observed a similar trend when they measured that the "average longest linear dimension" (ALLD) of the fines increased with successive refining.



Figure 9: Mass proportion of fibrillar fines in different fines fractions in the first and the second refining trials.

As indicated by both the images in Figure 8 and the measurements of the mass proportion of fibrillar fines in Figure 9, the morphology of the fines from the different refining stages varied. The fines produced in the second refining stage were more fibrillar and less flake-like than the ones produced in the first refining stage.

#### The chemical composition and the number of charged groups of the fines

The bulk composition of the different fines fractions was analysed and the results are shown in Figure 10. As the fines were produced in the later refining stages the amount of acid soluble and acid insoluble lignin was reduced. This was expected since there is a higher concentration of lignin in the outer layers of the fibre wall. The opposite trend was found for cellulose which increased as the fines were produced in the later refining stages.

The differences in bulk chemical composition between the different fines were surprisingly small when the quite large effect on the paper strength is considered. Others have also registered similar small differences in the bulk composition of different fines. For example, Luukko *et al.* (1999) registered a reduction in the lignin content from 34.6% to 31.2% of fines obtained from progressively refined TMP and Sundberg *et al.* (2003) measured the lignin content of flakes to be 39% whereas the fibrils contained only 33%. Heikkurinen and Hattula (1993) observed larger differences in the lignin content (between 39.0% and 28.8%) when mechanical pulp was refined six successive times. Different fines fractionated in a Bauer McNett apparatus showed small differences (Luukko *et al.* 1999, Paper IX).



Figure 10: The bulk composition of the fines from the second refining trial.

The carbohydrate composition of the different fines was analysed after depolymerisation by both acid hydrolysis and acid methanolysis (Paper II) and the amount of the individual carbohydrate monomers was quantified. The amount of the different carbohydrate monomers correlated well between the two methods with two important exceptions. First, uronic acids are decomposed during acid hydrolysis and are thus only possible to measure after acid methanolysis. Second, cellulose is only slightly degraded during acid methanolysis (Sundberg *et al.* 1996c). The amount of glucose quantified after the two de-polymerisation methods thus shows large differences. Since acid methanolysis only slightly degrades cellulose this method is well suited to measure the amount of hemicellulose and pectin.



Figure 11: The number of charge groups measured as polymer adsorption before and after alkali treatment compared to the number of uronic acids (glucuronic-, galacturonic and 4-O-methyl glucuronic acid) in different fines from the first refining trial.

The amount of uronic acids correlated well with the total amount of charged groups in the different fines fractions, as measured with polyelectrolyte titration using a low molecular weight cationic polymer at pH 8 (Figure 11). Other carboxylic acids like fatty

and resin acids, contributed only marginally to the total number of charged groups (Paper II). The three uronic acids glucuronic, 4-O-methyl glucuronic and galacturonic acid were measured after methanolysis. Galacturonic acid, which was the single most important contributor to the total number of charged groups, is mainly found as methylated esters in pectin. Since pectin is mainly found in the outer parts of the cell wall, higher amounts of this substance were expected to be found in the flake-like fines compared to the fibrillar fines. Figure 11 shows this was found by the measurements, and this result is supported by other authors (Sundberg *et al.* 2003). The number of charged groups, measured by polyelectrolyte titration, increased after alkali treatment which is probably a result of the demethylation and the creation of new carboxylic groups that occur with accessible ester groups at these conditions (Sundberg *et al.* 2003). Unexposed ester groups, like in triglycerides, are expected to be less affected since these hydrophobic components are reported to be unreachable for alkali and peroxide (Holmbom 2000).



Figure 12: The number of surface charged groups of the different fines from the first refining trial before and after alkali treatment.

The number of surface charged groups was measured with a high molecular weight polymer (poly DADMAC). The amount of charges accessible to the high molecular weight polymer is dependent on both the specific surface area and the charge density on the surface of the fines. The total charge was highest in the fines produced during the first refining as shown in Figure 11, but the opposite trend was observed for the surface charge. Figure 12 shows that the primary fines have the lowest surface charge, this is an apparent contradictory result which may be explained by differences in the specific surface or the content of the surface lignin and carbohydrates. Indeed, in Paper IV it is reported that flake-like fines have lower surface carbohydrate content than the bulk composition suggests. Furthermore, it can be assumed that flake-like fines have a lower specific surface area than fibril-rich fines, which also can explain the observed contradictory trends in the number of surface and total charge groups.

In conclusion, the various fines from the successive refining trials had both different chemical composition and number of charged groups. The flake-like fines contained more lignin and less carbohydrate compared to the fibrillar fines. It is largely because pectin is located in the outermost surface layer of the fibre, that the flake-like fines from the first refining stage contained more charged groups than the fibrillar fines

#### The surface composition and contact angles of fines

The surface composition of the fines was measured with ESCA (Electron Spectroscopy for Chemical Analysis) before and after 12 hours of hexane extraction. Hexane was chosen since it quite selectively extracts wood resin (Sundberg 1995) while other solvents like acetone, is known to also extract components like lignans and low molecular weight carbohydrates (Ekman 1980). It was important to have high selectivity when the wood resin was removed by extraction to avoid any artefacts. Removal of the carbohydrates during the extraction procedure would easily influence the result when a surface sensitive instrument like ESCA was used since this instrument only measures in the upper 5-10 nm layers of the surface (Laine *et al.* 1994b). The surface coverage of carbohydrates, lignin and extractives was calculated based on the results before and after extraction according to Luukko *et al.* (1999). Any wood resin that was not removed in the extraction stage would be interpreted as being lignin.



Figure 13: The surface composition of the different fines fractions from the second refining trial as revealed by ESCA.

The result of the ESCA analysis is shown in Figure 13. As the fines are produced at later refining stages the carbohydrate coverage on the surface increases from approximately 15 to 60%, while the coverage of extractives is reduced from approximately 30 to less than 1%. Others have also measured large variations in the surface composition between fines. Luukko and Paulapuro (1999b) measured the surface coverage of extractives on fines in a TMP process to be between 9.6 and 50.6% while the total amount of extractives varied between 0.7 and 2.3%. Kleen *et al.* (2001) measured the surface content of extractives on fines to be between 13 and 19%, while the bulk content of extractives in the fines was between 0.37 and 0.4%. In both cases ESCA was used to measure the surface composition. Assuming that this method measures the correct surface composition, the bulk composition of fines is not representative of the surface composition. This may explain the large differences in the

properties of the different fines, despite the small differences in the bulk composition (Figure 10).

A possible explanation for the difference in the surface and the bulk composition may be the adsorption or desorption of carbohydrates or wood resin in water suspensions. Sundberg (Paper IX) showed that galactomannan adsorbed to fibrillar fines ( $\sim$ 50% of the added galactomannan), while only minor amounts adsorbed to flake-like fines (less than 5%).

The contact angles between the fines and different liquids (water, tetrabromoethane (TBE) and formamide) are shown in Table 2. The table shows how the contact angles between the fines and polar liquids like water or formamide was reduced as the fines were produced in later refining stages. The contact angle between the fines and the unpolar liquid TBE showed minor variations which was expected since the dispersive component of the surface tensions of cellulose, lignin and wood resin are reported to be similar (Nylund *et al.* 1998; Shen *et al.* 1998). This indicates that the sheet structure did not influence the measurements significantly and that the variation in contact angles between the fines and the polar liquids probably was caused by variation in the hydrophobicity of the fines.

| water, tetrabromoethan | e (TBE) and formam | nide.          |                |
|------------------------|--------------------|----------------|----------------|
| <b>Fines fraction</b>  | Contact angle,     | Contact angle, | Contact angle, |
|                        | water (°)          | TBE (°)        | formamide (°)  |
| Flake-like fines       | 109                | 25             | 70             |
| First fibrillar fines  | 62                 | 19             | 25             |

24

18

57

Second fibrillar fines

Table 2: The contact angle after 0.2 s between the pure fines sheets and the liquids water, tetrabromoethane (TBE) and formamide.

The large variation in the surface composition reflects to a certain extent the measured contact angles in Table 2. The largest contact angle was between the flake-like fines and water ( $109^{\circ}$ ) which also had the highest content of extractives and lignin on the surface. These are surprisingly large contact angles, but other authors have also reported large values. Rundlöf *et al.* (2000) measured the contact angles of fines and water to between 96° and 101°. Large contact angles have also been measured between water and laboratory paper made from unbleached TMP. After the addition of steryl esters which are important components in wood resin, contact angles rose from less than 40° to more than 100° (Kokkonen *et al.* 2002).

In conclusion, the analysis of the surface composition using ESCA and the contact angle measurements showed that there were large variations in the surface properties between the different fines and that these variations were larger than what would be expected from the bulk composition measurements.

# The effect of the different types of fines, colloidal wood resin and salt on properties of laboratory sheets

One important property of the fines in mechanical pulp is their effect on the paper quality, particularly the paper strength. Fibrillar fines are known to contribute to stronger paper, among other things, compared to the flake-like fines. The effect of the fines from the successive refining trials on paper quality was tested by producing laboratory sheets from a blend of the fines (30%) and mechanical pulp fibres free of fines (Papers IX and X). In addition, the effect of salt and model colloidal extractives on the paper quality was measured. This was measured as the effect of adding salt (NaCl, 4 g/L) or model colloidal extractives (~110 mg/L) on the paper strength. Figure 14 presents the results of these trials. The figure also shows that the tensile index was low when the fines were flake-like (Paper IX) and that as more fibrillar fines were used better bonding and higher strength of the laboratory sheets were achieved. Other strength parameters like Scott bond and tear index (not shown) gave the same result. The effect of the different types of fines on the paper properties correlates well with the results reported by other authors (see for example Retulainen *et al.* 1993; Luukko and Paulapuro 1999a).



Figure 14: The tensile indexes of the laboratory sheets. Open symbols refer to using tap water as model process water. The grey symbols refer to the addition of salt, and the black symbols refer to the addition of wood resin. The error bars show the 95% confidence limits.

Figure 14 also illustrates the effect of adding salt or model colloidal extractives on the tensile index of the laboratory sheets. Since salt screens charged groups and thus reduces the swelling pressure a decrease in the paper strength could be expected. As seen in Figure 14 this effect was detected, particularly when the flake-like fines with a high number of charged groups were used. The added colloidal wood resin, which was to some extent retained in the sheet (Table 3), had a significant detrimental effect on the strength properties of all the laboratory sheets (Figure 14). Since the hydrophobic wood resin retained in the sheet inhibits the creation of bonds between fines or fibres, all the strength parameters were affected negatively. Scott bond, which is a measure of the internal strength (bonding ability) of the paper, was markedly (50-60%) reduced compared to the sheets made without any addition. Another consequence of reduced

bonding, as a result of either colloidal extractives or flake-like fines, is an expected increase in phase boundaries. A measured increase in the light scattering coefficient and air permeability confirmed this (Paper X).

Table 3 shows the amount of extractives in the different laboratory sheets after the addition of either salt or model colloidal wood resin. When the colloidal wood resin was added the amount of extractives in the sheet increased but since the laboratory sheets were made without retention or fixation aids, only approximately 10% of the added wood resin was retained in the sheet. For comparison, Kokkonen *et al.* (2002) reported of the retention of model compounds in the laboratory sheets in the range of 15 to 50%.

| Type of<br>fines (30%<br>in sheets) | Addition    | Total fatty<br>acids | Resin<br>acids | Sterols | Total<br>extractives | Contact<br>angle with<br>water (°) |
|-------------------------------------|-------------|----------------------|----------------|---------|----------------------|------------------------------------|
|                                     | No addition | 0.38                 | 0.03           | 0.22    | 0.63                 | 86                                 |
| flake-like                          | Salt        | 0.30                 | 0.03           | 0.12    | 0.45                 | 93                                 |
| lines                               | Wood resin  | 3.42                 | 1.17           | 1.57    | 6.16                 | 95                                 |
|                                     | Water       | 0.10                 | 0.02           | 0.05    | 0.18                 | 56                                 |
| first fibrillar                     | Salt        | 0.12                 | 0.02           | 0.06    | 0.21                 | 52                                 |
| lines                               | Wood resin  | 3.20                 | 1.50           | 1.65    | 6.35                 | 83                                 |
|                                     | Water       | 0.08                 | 0.02           | 0.05    | 0.14                 | 49                                 |
| second                              | Salt        | 0.11                 | 0.02           | 0.04    | 0.18                 | 50                                 |
|                                     | Wood resin  | 2.24                 | 1.81           | 0.95    | 5.00                 | 97                                 |

Table 3: The amount of extractives (mg/g) in the laboratory sheets. The amount of extractives in the laboratory sheets had an effect on the surface hydrophobicity of the sheets, measured as the contact angle against water after 0.2 s.

The addition of wood resin changed the contact angle between the water and the paper surface. This increase in the contact angle is probably caused by an increase in the hydrophobicity of the paper surface. Similar effects have been reported by Kokkonen *et al.* (2002) who found that model lipophilic extractives increased the contact angle of laboratory sheets. Table 3 shows that the added wood resin increased the contact angle of the papers primarily when fibrillar fines are used. In these sheets the contact angle towards water increased from  $49-56^{\circ}$  to  $83-97^{\circ}$  after the addition of wood resin while the increase in the contact angle between water and the sheets containing flake-like fines was much smaller (from  $86^{\circ}$  to  $95^{\circ}$ ). A possible explanation is that the flake-like fines have a more hydrophobic surface than the fibrillar fines, and thus the effect on the surface hydrophobicity of adding wood resin is reduced.

In conclusion, the fines from the successive refining trials had a significant effect on the properties of laboratory sheets. The flake-like fines reduced the strength of laboratory sheets and increased the hydrophobicity while the fibrillar fines had the opposite effect. Colloidal wood resin affected the laboratory sheets similar to the flake-like fines while the addition of salt had minor effects.

# 3. Swelling of the fines after chemical treatment (Paper III)

The swelling of fines is important because it influences the dewatering of the paper machine during papermaking and contributes to the strength of the paper. The main aim of the measurements was to determine if different chemical treatments affected the swelling properties of the fines. As shown by Equations 1 and 2 this could be done by either changing the number of charged groups or changing the elasticity of the fines. Modification of the rigid lignin would possibly change the elasticity of the fines and hence the swelling behaviour.

The swelling of fines was measured as fibre saturation point (FSP) using a large dextran polymer. Prior to the swelling measurements the fines were either untreated, alkali treated or peroxide bleached. After the treatments the carboxylic acid groups in the fines were converted to either their H-forms or Na-forms before the FSP was measured, and the results are shown in Table 4.

Table 4: The swelling of different fines from the second refining trial (as FSP values), and the difference between the swelling measured at pH 2 and pH 5.4 ( $\Delta$ FSP). The fines were untreated, alkali treated or peroxide bleached. The standard deviations (N = 3 or 4) are given in parentheses.

| Type of fines and treatment              | FSP at pH 2  | FSP at pH    | ∆FSP<br>between nH |
|--|--------------|--------------|--------------------|
|  |              | 5.4          | 5.4 and pH 2       |
| flake-like fines untreated               | 0.85 (0.04)  | 0.98 (0.03)  | 0.13               |
| first fibrillar fines untreated          | 0.94 (0.03)  | 0.98 (0.08)  | 0.04               |
| second fibrillar fines untreated         | 0.87 (0.08)  | 0.98 (0.06)  | 0.11               |
| flake-like fines alkali treated          | 0.94 (0.06)  | 1.03 (0.14)  | 0.09               |
| first fibrillar fines alkali treated     | 0.87 (0.14)  | 1.03 (0.08)  | 0.16               |
| second fibrillar fines alkali treated    | 1.07 (0.08)  | 1.17 (0.004) | 0.10               |
| flake-like fines peroxide bleached       | 0.95 (0.004) | 1.44 (0.05)  | 0.49               |
| first fibrillar fines peroxide bleached  | 1.02 (0.05)  | 1.43 (0.04)  | 0.41               |
| second fibrillar fines peroxide bleached | 0.96 (0.04)  | 1.30 (0.13)  | 0.34               |

There were small, if any, differences in the degree of swelling between the different fines fractions. Since swelling is a physico-chemical property which is dependent on the bulk composition, the small degree of swelling was reflected by the small variation in the bulk composition between the different fines (Figure 10). In contrast, Luukko and Maloney (1999) found a clear correlation between the amount of fibrillar material and the degree of swelling. A possible explanation is that the fibrillar content in these measurements varied between 35 and 48%, whereas Luukko and Maloney (1999) had a variation between 30 and 80%. This smaller variation, in addition to a larger standard deviation, may have caused this lack of correlation between swelling and amount of fibrillar material.

Generally, as expected, the swelling is lower at pH 2 (H-form of the carboxylic acids) than at pH 5.4 (Na-form of the carboxylic acids). After alkali treatment, which presumably increased the amount of charged groups at pH 5.4 (Paper II, Sundberg *et al.* 

2000a, Sundberg *et al.* 2003), the swelling of the different fines was only slightly changed. An increased amount of charged groups increases the swelling pressure (Equations 1 and 2), but this did not result in significantly more swollen fines. A likely explanation is that the lignin, which is not very elastic, prevented the swelling of the fines. Only peroxide bleaching affected the fines in such a way that there was a substantial increase in the swelling. By calculating the  $\Delta$ FSP values, this effect was pointed out. Peroxide bleaching is known to affect the lignin, either by introducing new charged groups (Gellerstedt *et al.* 1980) or by cleaving covalent bonds by the Dakin-reaction (Dence 1996). A change in the lignin structure, resulting in either an increased elasticity and/or new charged groups in the lignin could have caused this increased swelling. According to Sundberg *et al.* (2000a) the major part of the increase of charged groups in mechanical pulp after peroxide bleaching is attributed to the demethylation of ester groups, which is an effect of the alkali rather than the peroxide itself. Thus, unlike the alkali treatment shown in Table 4, at least some of the increased swelling after peroxide bleaching may be attributed to a change in the elasticity of the lignin.

### 4. Adsorption of model colloidal extractives to fines (Paper IV)

There were two main aims with the measurements of the adsorption of model colloidal extractives to the different types of fines. The first aim was to determine at what conditions such adsorption occurred and the second aim was to determine if there was any selectivity in such adsorption. Selective adsorption to low-bonding flake-like fines is often wanted because the removal of the dispersed wood resin with the paper becomes less detrimental to the paper strength.

The adsorption measurements of model colloidal extractives to the different fines were first done in very simple systems. In the adsorption measurements without the addition of dissolved substances no selectivity in the adsorption of the wood resin to the different fines was detected. The flake-like fines and the fibrillar fines adsorbed the colloidal wood resin in a similar way. Whether or not adsorption occurred depended on the degree of electrostatic stabilisation. The electrostatic stability of the colloidal wood resin was manipulated either by reducing the net surface charges or by screening the surface charges. The first was done by lowering the pH to substantially below the pKa of the surface acid groups and the last was done by adding a simple electrolyte (NaCl). Consequently, at pH values below approximately 5 or at an increased salt content the stability of the colloidal wood resin was reduced and adsorption to the fines occurred (Figure 15 adapted from Paper VIII).



Figure 15: Adsorption of colloidal extractives to different fines (from the second refining trial).

In addition to the electrostatic stabilisation, the colloidal wood resin in process water is also stabilised sterically by dissolved substances (Sundberg *et al.* 1996b). In process water both the electrostatic and the steric stabilisation will thus influence the adsorption of the colloidal wood resin to fines. The effect of these dissolved substances on the adsorption behaviour of the colloidal wood resin to the different fines was thus investigated more thoroughly (Paper IV). First the removal kinetics and the amount of dissolved substances needed to avoid any removal or adsorption of the colloidal wood resin to fibrillar fines was determined (Figure 16). In these trials only the dissolved substances provided the colloidal stabilisation since the low pH (pH = 2.3) caused minor, if any, electrostatic stabilisation (Paper IV). As shown in Figure 16 the dissolved substances prevented the removal of the colloidal wood resin from solution.



Figure 16: The adsorption of model colloidal wood resin to the second fibrillar fines from the second refining trial at different additions of dissolved substances (pH = 2.3).

The relative amount of dissolved substances needed to sterically stabilise the colloidal wood resin was in the range 3:1 (w:w), measured as the carbohydrate-to-resin ratio. The amount of carbohydrates could be used as a measure of the amount of dissolved substances since the carbohydrates, which are mainly present as oligo- or polysaccharides, were the main constituent of the dissolved components (Papers IV, V and VI). The assumption that the carbohydrates were mainly present as oligo- or

polysaccharides is justified by the fact that the solution was dialysed for a minimum of two days using a dialysis membrane (Spectra/Por 4) which removes mono-, di-, tri- and tetrameric polysaccharides (Knutsen *et al.* 1993).

The main carbohydrates, measured as monosaccharides, were mannose (Man), glucose (Glc) and galactose (Gal). These three monomers are the main constituents in galactoglucomannan and the ratio between them (Man:Glc:Gal) were found to be 3.5:1:0.8 (Paper IV), 3.1:1:0.8 (Paper V), 4.2:1:1.0 (Paper V) and 3.4:1:0.9 (Paper VI). These values are close to what is found in the literature for water-soluble galactoglucomannan (3:1:1, Fengel and Wegener 1989) and reported for neutral polysaccharides dissolved from TMP (4:1:0.6, Thornton *et al.* 1994).

Since the stabilising effect of the dissolved carbohydrates depends on the size (or degree of polymerisation, DP) the number average DP was calculated by dividing the total amount of dissolved carbohydrates with the amount of reducing ends. This resulted in a number average DP between 45 (8200 g/mole) and 53 (9500 g/mole) which is close to what has been estimated to be the size limit for steric stabilisation by polymers. It has been estimated (Napper 1983) that for steric stabilisation of colloidal droplets by carbon backbone polymers a minimum molecular weight of around 10000 is required.

The sterically stabilised colloidal wood resin was quite stable since it did not easily precipitate or adsorb to surfaces. In order to achieve sufficient adsorption the sterical and/or electrostatic stabilisation had to be reduced. This could be done either by reducing the concentration of the dissolved substances, screening the charged groups by adding simple electrolytes (for example NaCl) or removing the charged groups by lowering the pH substantially below the pKa-value for the carboxylic acids. In all of the three cases the flake-like fines adsorbed the colloidal wood resin more effectively than the fibrillar fines (Paper IV). Figure 17 illustrates the adsorption of the sterically stabilised model colloidal wood resin by the different fines after the addition of 0.1 M NaCl.



Figure 17: The adsorption of colloidal extractives to different fines fractions from the second refining trial after steric stabilization with dissolved substances (carbohyd./resin 3:1) and the addition of 0.1 M NaCl.

#### Estimation of the specific surface area of the fines

Measuring the specific surface of different types of fines is ambiguous, and the result is dependent on the method used. Gas adsorption has been used, but requires drying of the fines, which results in a loss of specific surface. If, for example, only the surface accessible to the colloidal wood resin is of interest, the gas adsorption also measures surfaces inside very small pores (2-3 nm) that are inaccessible to colloidal extractives. In fibres from groundwood pulp and TMP, and possibly also in fines, almost all of the pores are smaller than 200 nm (Maloney and Paulapuro 1999) making them too small for the colloidal wood resin to enter.

Turbidity (T) has been reported to be a convenient way to determine the specific surface (SS)s in solution (Wood and Karnis 1996), and the relation between turbidity and specific surface was reported to be

#### T = K x concentration of fines x (SS)s Equation 12

The turbidity of the fines at different concentrations was measured (Figure 18), and the response factor calculated. The water content of the fines (FSP) was measured to be approximately 0.98 g water/g fines. By following the calculations of Wood and Karnis (1996) the constant K in Equation 12 becomes 1.27 FTU/(% m<sup>2</sup>/kg), which gives a specific surface of 13 m<sup>2</sup>/g and 15.5 m<sup>2</sup>/g for the flake-like and the fibrillar fines, respectively. For comparison, Wood and Karnis (1996) estimated a specific surface of about 13 m<sup>2</sup>/g for P200 groundwood fines.



Figure 18: The turbidity of fines from the second refining trial at different concentrations.

It is also possible to use geometrical considerations to estimate the specific surface. Flake-like material from the middle lamella and the fibrillar material from the secondary wall have a reported thickness in the wet state of approximately 0.56  $\mu$ m and 0.33  $\mu$ m respectively (Boutelje and Eriksson 1984). Heikkurinen and Hattula (1993) have reported that the average longest linear dimension of fines produced during successive refining trials is 17.0  $\mu$ m for the first fines and 48.7  $\mu$ m for the last fines. Using these figures as the length of the fines together with the thickness and assuming a width of 5  $\mu$ m, a pure geometric calculation will give a specific surface of the flake-like fines of approximately 3.1 m<sup>2</sup>/g and 5.0 m<sup>2</sup>/g for the fibrillar fines.

The two estimates gave large differences in the range of the specific surface, but both approaches estimated that the flake-like fines had a lower specific surface than the fibrillar fines.

#### Causes of the differences in adsorption efficiency between the fines

The higher adsorption efficiency of the flake-like fines compared to the fibrillar fines was probably not caused by a variation in the specific surface. As discussed above, the fibrillar fines probably have a larger specific surface than the flake-like fines. If the surface chemistry of the fines is not important, the fibrillar fines should thus be able to adsorb the colloidal extractives more effectively than the flake-like fines, but the opposite was observed. The large variation in the surface composition of the different fines (Figure 13) seems thus to have a clear effect on the adsorption efficiency.

The higher adsorption efficiency of the flake-like fines may be caused by them having a more hydrophobic surface compared to the fibrillar fines (Table 2). This would make them more capable of adsorbing hydrophobic wood resin, as was observed. An alternative explanation is that there are more anchored carbohydrates with solvated tails on areas covered by carbohydrate compared to areas covered by lignin or wood resin. These tails, which are partly in solution, would thus create a steric shield preventing the colloidal extractives to adsorb onto the surface.

Potential desorption of the adsorbed colloidal wood resin was measured by increasing the pH in the surrounding liquid phase after the colloidal wood resin had been adsorbed. Little, or nothing, of the adsorbed colloidal wood resin was desorbed (maximum 12%).

# 5. Effects of polymers and fines on the removal of colloidal wood resin (Paper V)

There were two main aims in the experiments using different polymers and different fines to remove model colloidal from solution. The first aim was to determine if any of the commercially available polymers had the ability to adsorb, or fix, the model colloidal to certain fines and not to others ("targeted fixation"). The second aim was to determine if the dissolved material influenced this property.

#### **Removal experiments with PEO and CPAM**

The two commercially available polymers polyethyleneoxide (PEO) and cationic polyacrylamide (CPAM) were used in the removal experiments. As expected both polymers had the ability to remove sterically stabilised model colloidal wood resin from solution when fines were present (Figures 19a and 19b). When PEO was used in this way it was possible to remove the model colloidal wood resin from solution much more efficiently when flake-like fines were present compared to when the fibrillar fines were present (Figure 19a). As shown in Figure 19b, CPAM did not have this selective effect (Paper V).



Figure 19a: Removal of sterically stabilised model colloidal wood resin from solution with PEO and two different types of fines (flake-like fines and second fibrillar fines).



Figure 19b: Removal of sterically stabilised model colloidal wood resin from solution with CPAM and two different types of fines (flake-like fines and second fibrillar fines).

The minimum shown in Figure 19a is sometimes termed the "optimum polymer dose" (OPD) (se for example Sundberg et al. 1993) which is the polymer dose needed to obtain maximum removal of colloidal wood resin. The residual turbidity increased by increasing the polymer concentration after OPD which indicated that above this concentration the added polymer participated in the steric stabilisation of the colloidal wood resin or the surface of the fines. The addition of large amounts of CPAM had a similar effect (not shown).

#### Adsorption of PEO to fines and extractive surface

As PEO was able to remove colloidal wood resin from solution primarily when the flake-like fines were present, the polymer must have affinity to both the surfaces of the wood resin and the flake-like fines. Using the same argument, the affinity of PEO to the fibrillar fines should be considerably lower than to the flake-like fines. This selectivity in the adsorption of PEO was measured, and the results are shown in Figure 20. The figure shows that PEO was adsorbed by the different fines to a plateau level, but this plateau level was significantly higher for the flake-like fines than for the fibrillar fines. Such distinct differences in the adsorption level by the various types of fines may be explained by the differences in the surface composition. As shown in Figure 13, the flake-like fines have a higher content of surface lignin and extractives than the fibrillar

fines. As PEO is reported to have affinity towards phenolic groups (Van de Ven 2000), which are mainly found in lignin, the difference in the adsorption of PEO by different fines was expected. PEO was also shown to have affinity to hexane extract (shown below), and as shown in Figure 13 the surface coverage of extractives on the flake-like fines was much higher compared to the fibrillar fines.

This difference in affinity towards the different types of fines may lead to asymmetric bridging, as suggested by Carignan *et al.* (1998). Asymmetric bridging means that PEO adsorbs only to one type of fines and not to other types of fines or particles. After the initial adsorption, the affinity of the non-adsorbed parts of the PEO molecules towards other particles in solution, such as the other type of fines increases, due to the initial loss of entropy. This may occur when the different types of fines are blended.



Figure 20: The adsorption of PEO to different types of fines.

As shown in Figure 20, the amount of adsorbed PEO to the flake-like fines was approximately 0.8 mg/g and between 0.2 and 0.4 mg/g to the fibrillar fines. For comparison, the amount of PEO adsorbed to unbleached kraft fibres has been shown to be maximum 0.6 mg/g (Picaro and Van de Ven 1995). The amount of PEO adsorbed to the fines was thus lower than expected. First, because the specific surface of the fines is considerably larger than of kraft pulp which suggests that fines should adsorb more PEO. Second, because the amount of surface lignin, which probably is the most important adsorption site, is reported to be in the range of 15% (Laine *et al.* 1996) for unbleached kraft pulp (kappa number 25). The content of surface lignin on the different types of fines varied between 39% and 55% (Figure 13) which suggests that the fines should be able to adsorb more PEO than the kraft pulp. The low adsorption of PEO to the fines compared to the kraft pulp may thus be explained by other circumstances which could be the differences in the properties of the surface lignin or the surface extractives.

The ability of PEO to remove the sterically stabilised colloidal material in the presence of fines suggests there was some affinity between the colloidal wood resin and PEO.

This affinity was determined by measuring the adsorption of PEO to a flat surface of hexane extract using a QCM-D instrument (Figures 21 and 22).



Figure 21: The adsorption of dissolved substances and PEO to the extractives surface shown as a change in the resonant frequency,  $\Delta f$ , vs time at 15 MHz.



Figure 22: The effect of the concentration of the dissolved substances (DS) on the adsorption of PEO to the extractives surface.

Figure 21 shows that dissolved substances (DS) were adsorbed to the extractives surface and that the adsorption increased with a higher concentration of the dissolved substances. The latter was seen as a stronger reduction in frequency. This is not surprising since these substances are known to sterically stabilise extractives in the colloidal form (Sundberg *et al.* 1996b; Papers IV and V). As the amount of adsorbed dissolved substances increased, the tendency of adsorption of PEO to the extractives surface decreased. This can be observed as a smaller change in frequency after the addition of PEO and is illustrated in Figure 22. The figure shows the change in frequency after the addition of PEO, plotted as a function of the concentration of dissolved substances. When the concentration of dissolved substances increased to 100 mg/L, there was very little change in the frequency after the PEO addition, *i.e.* hardly any PEO was adsorbed to the extractives surface. The dissolved material which is adsorbed is assumed to be carbohydrates since they sterically stabilise colloidal wood resin (Sundberg *et al.* 1996b). Assuming that the adsorbed material is polysaccharides, these adsorbed carbohydrates may create a carbohydrate layer on the surface of the extractives which seems to prevent the succeeding adsorption of PEO. One explanation of this effect may be that it is known that PEO does not adsorb to surfaces of carbohydrates. As an example, bleached kraft pulp which has a surface that is almost completely covered with carbohydrates (Laine *et al.* 1994b) does not adsorb PEO (Picaro and Van de Ven 1995).

In contrast to the results presented here, Kekkonen *et al.* (2002) show that model colloidal wood resin does not adsorb to silica surfaces that are pre-adsorbed with PEO. Adsorption of dissolved and colloidal substances (DCS), however, occurs. There may be differences in the composition between colloidal wood resin used by Kekkonen *et al.* (2002) and the hexane extract used here. Small lignin impurities containing phenol in the hexane extract would probably enhance the affinity between the extract and PEO.

### 6. Adsorption of model colloidal extractives to fillers (Paper VI)

There were two main aims in measuring the adsorption of model colloidal wood resin to fillers. The first aim was to determine whether this adsorption occurs on the fillers investigated and use estimated interfacial energy in order to try to explain the adsorption. The second aim was to determine if such an adsorption is influenced by dissolved substances.

#### **Adsorption measurements**

The removal of model colloidal wood resin from solution with different fillers present is shown in Figure 23. Independent of which filler that was used, the removal efficiency increased with the concentration of the filler. Without the addition of filler or dissolved substances the electrostatically stabilised model colloidal wood resin was stable in the buffer solution (pH = 5.4, I = 0.01M). After 25 hours the residual turbidity after centrifugation was virtually unchanged (from 268 to 258 NTU).



Figure 23: The effect of dissolved substances (as the ratio of carbohydrates to colloidal extractives, w/w) on the adsorption of colloidal extractives to fillers at pH 5.4.

An increase in the concentration of dissolved substances resulted in more colloidal extractives in the supernatant, meaning that the adsorption of colloidal wood resin decreased. The composition of the dissolved substances was similar to what was used in the adsorption study of model colloidal wood resin to fines and the results of a chemical analysis is presented in Paper VI. The dissolved substances which stabilise colloidal wood resin sterically (Sundberg *et al.* 1996b) also reduced the adsorption to different fillers, as the results in Figure 23 suggest. This may be caused by the dissolved substances being adsorbed to the model colloidal wood resin or to the fillers.

When the amount of dissolved substances increased, the fillers were less able to sediment. This may be seen in (Paper VI, Figure 2), where the turbidity increases with the concentration of fillers at a carbohydrate-to-resin ratio of 8:1. This suggests an affinity between the dissolved substances and fillers, which also has been observed by Willför *et al.* (2000). This affinity is shown more clearly in (Paper VI, Figure 2). Here, as the amount of dissolved substances increased, the sedimentation of the fillers was less effective. In the latter case no colloidal wood resin was added. The fact that the

fillers sedimented less after the addition of the dissolved substances does not change the general conclusion from Figure 23 since the contribution to the turbidity from the fillers in solution is too low.

#### Contact angle measurements and interfacial tension

The contact angles between wood resin and different liquids were measured, and the surface energy was calculated using Equation 9. The results are presented in Table 5. The model colloidal extractives originated from hexane extract, and the measured and calculated surface energy values from the acetone extract are presented for comparison only. As shown in Table 5 the main contribution to the total surface energy of the hexane extract is the Lifshitz-van der Waals contribution. The polar contribution, calculated using Equation 10, was minor ( $\gamma^{AB} = 2 \cdot \sqrt{\gamma_1^+ \cdot \gamma_1^-} = 2.3 \text{ mJ/m}^2$ ). By comparison, the acetone extract had a higher  $\gamma^{AB}$  (6.8 mJ/m<sup>2</sup>) and lower  $\gamma^{LW}$ . A possible explanation for this is that in addition to wood resin, acetone may also extract lignans and low molecular weight carbohydrates (Ekman 1980).

The surface energy of the extract is assumed to be similar to the same material dispersed in water. This is of course a rather daring assumption, but it is to some extent justified as the composition of hexane extract has been shown to be very similar to the composition of colloidal material made from hexane extract (Sundberg *et al.* 1996a). This suggested that all the extracted compounds were equally dispersed. A source of error is that the composition on the surface may be different from the bulk composition of the hexane extract and the colloidal droplets are not similar.

The work of adhesion between water and hexane extracted wood resin was calculated using Equation 3, resulting in  $Wa_{rw} = 104 \text{ mJ/m}^2$ , which is close to the value 100 mJ/m<sup>2</sup> obtained by Nylund *et al.* (1998). By combining Equations 5, 7 and 9 the energy of interaction was estimated ( $\Delta G_{rwr}/area = -38.8 \text{ mJ/m}^2$ ), and the result indicates that the adsorption of colloidal wood resin to other colloidal wood resin droplets in water is energetically favourable. Thus, the wood resin stays as colloidal droplets because they are stabilised, electrostatically and/or sterically.

Table 5: The different contributions to the surface energy  $(mJ/m^2)$  of wood resin. The wood resin was either extracted with hexane or acetone.

|                 | $\gamma_r^{LW}$ | $\gamma_r^+$ | $\gamma_r$ | $\gamma_r^{tot}$ |
|-----------------|-----------------|--------------|------------|------------------|
| Hexane extract  | 48.3            | 0.1          | 12.8       | 50.6             |
| Acetone extract | 41.2            | 0.3          | 38.0       | 48.3             |

The surface energy of the talc and kaolin (literature data) are shown in Table 6. It was not possible to obtain data for the Mg-Al-silicate.

|        | $\gamma_f^{LW}$ | $\gamma_f^+$ | $\gamma_f$ | $\gamma_f^{tot}$ | reference             |
|--------|-----------------|--------------|------------|------------------|-----------------------|
| Kaolin | 35.9            | 0.4          | 34.3       | 43.3             | Constanzo et al. 1991 |
| Talc   | 31.7            | 1.8          | 3.9        | 37.0             | Constanzo et al. 1991 |
| Talc   | 29.7            | 0.5          | 6.1        | 33.2             | Yordan et al. 2001    |

Table 6: The different contributions to the surface energy  $(mJ/m^2)$  of fillers.

There are two sets of values for the surface energy of talc, which are fairly similar. In both cases the constants are measured using a thin layer wicking technique where the migration of different liquids through a layer of the filler particles is measured and the surface energy calculated. Using the values in Tables 5 and 6 (Yordan *et al.* (2001) provide the values for talc) and Equations 2, 4-6, it is possible to calculate the free energy of interaction between the model colloidal wood resin and the fillers ( $\Delta G_{fwr}$ ). These results are shown in Table 7, and all the values are negative. Negative values indicate that there is a net free energy of interaction between the colloidal wood resin and the fillers investigated.

*Table 7: The free energy of interaction between the model colloidal extractives and the fillers.* 

|        | $\Delta G_{fwr} (mJ/m^2)$ |
|--------|---------------------------|
| Kaolin | - 11.4                    |
| Talc   | - 40.8                    |

Despite the negative  $\Delta G_{rwr}$  values (-38.8 mJ/m2), the colloidal wood resin stayed dispersed. In contrast, adsorption of the model colloidal extractives to the fillers occurred at low levels of dissolved substances. The fillers thus seem to enhance the removal of the colloidal wood resin from solution. At least for kaolin, one explanation may be that the cationic edges of the filler reduces the net effect of the electrostatic repulsion, in other words, they lower the energy barrier between the surfaces. The lowered energy barrier may thus increase the adsorption rate between the fillers and the model colloidal wood resin compared to the adsorption rate between the model colloidal wood resin.

The measured adsorption of model colloidal wood resin to fillers presented in Figure 23 is energetically possible, as indicated in Table 7. The difference in the magnitude of the free energy of interactions between the model colloidal wood resin and the two fillers talc and kaolin was not reflected in any observed difference in adsorbing ability. The different fillers seemed to adsorb the model colloidal wood resin in a similar manner.

# **Concluding remarks**

#### Extraction of hydrophobic material from process water

The developed solid phase extraction (SPE) procedure can be used to extract fatty acids, resin acids and sterols from white water. The extraction efficiency is comparable to liquid-liquid extraction using methyl tert.-butyl ether (MTBE) as an organic solvent. Plugging of the SPE column was only solved to some extent by the addition of acetone.

#### Analysis of the chemical composition and the number of charged groups of fines

The fines produced early in the first refining stage had a higher number of charged groups than the fines produced in later refining stages. A reduced demand of cationic fixatives per gram fines may therefore be expected with prolonged refining. Galacturonic acid, which is the main carbohydrate monomer in pectin, was largely responsible for this difference. The three uronic acids, galacturonic acid, glucuronic acid and 4-*O*-methyl glucuronic acid, contributed to between 80 to 90% of all the charged groups in the different fines measured as polymer adsorption. The charged groups in fatty and resin acids did not contribute significantly in this case. The number of surface charged groups on the different fines varied less, but in an opposite manner compared to the total number of charged groups. The fines that were produced in the first refining stage had a lower surface charge than the fines produced in later refining stages. This may be a consequence of differences in the specific surface or a result of the surface content of lignin.

The surface composition of the fines, as measured by ESCA, did not reflect the bulk composition. There were much larger variations in the surface composition between the fines compared to the bulk composition. This was reflected by large variations in contact angle measurements between the fines.

#### Adsorption of model colloidal extractives to fines

The adsorption of model colloidal wood resin to fines was strongly dependent on the degree of colloidal stabilisation. The pH, the ionic strength and the concentration of dissolved substances greatly influenced the adsorption. At certain conditions there was a difference in the ability of fines to adsorb colloids. At low pH value (pH 2.3), high ionic strength (I=0.1M) or at low concentration of dissolved substances the fines that were rich in flakes and ray cells showed a stronger ability to adsorb the colloidal extractives than the more fibrillar fines.

#### Effects of polymers and fines on the removal of colloidal extractives

The effect of different types of fines and polymers on the removal of model colloidal wood resin from solution has been demonstrated. When PEO was used together with different types of fines the removal was more effective when flake-like fines were present compared to fibrillar fines. Adsorption of PEO to the different fines showed a clear preference towards the flake-like fines. This may be caused by the higher lignin

content, or lower carbohydrate content, on the surface of the flake-like fines compared to the fibrillar fines. Adsorption of PEO to extractives was also measured. The adsorption of PEO was inhibited at high amounts of adsorbed dissolved components to the extractive surface.

#### Adsorption of model colloidal extractives to fillers

Colloidal wood resin adsorbed to the three fillers investigated. This adsorption was reduced with an increasing amount of dissolved substances, probably caused by increased steric stabilisation of the colloidal wood resin. The dissolved substances also reduced the ability of the fillers to sediment during centrifugation. This indicates affinity, or adsorption, between the dissolved substances and the fillers.

Contact angle measurements and literature data indicated that both adsorption of colloidal wood resin to fillers and to other colloidal wood resin droplets was thermodynamically favourable but only adsorption to fillers occurred. This may be due to the amphoteric properties of the fillers where the cationic edges of the fillers lowered the electrostatic repulsion towards the negatively charged model colloidal wood resin.

# Some recommendations

#### Some consequences for the pulp- and paper industry

The low bonding flake-like fines may adsorb colloidal wood resin and may thus be a strategy for removing the colloidal wood resin from the process water without reducing paper strength. When circulating in the process water the fines will consequently become even more hydrophobic and contribute even less to the strength of the paper, but this negative effect is reduced if the wood resin is adsorbed to the low-bonding fines rather than to the bonding fibrillar fines. This specific adsorption is thus wanted and may be enhanced by the use of the commercial polymer polyethyleneoxide (PEO). This polymer adsorbs more to the flake-like fines than to the fibrillar fines, but the adsorption to wood resin is inhibited by dissolved components. This may be the reason why PEO has a reputation of being an "unstable" retention aid. PEO used for selective adsorption may then only be used in rather clean systems with a low concentration of dissolved components in the process water.

Fillers may also be used to remove the colloidal wood resin from the process water. The colloidal wood adsorbs to fillers which in any case does not contribute to the strength of the paper. Unfortunately this adsorption is also inhibited by dissolved components. This strategy is thus efficient at low concentrations of dissolved components.

#### Further work on the stabilisation of colloidal wood resin

It is very clear that the dissolved material from mechanical pulp contribute to a stable colloidal wood resin. Usually it is assumed that glucomannan is a large contributor to this stabilisation, mainly because it is the most abundant wood polymer present in the suspension. A group of dissolved components like lignosaccharides (LCC) are probably effective in the stabilisation because it has a hydrophilic (lignin) and a hydrophilic group (carbohydrate). Analytical procedures to measure LCC in water and more thorough investigations on the effects of LCC on stability of colloidal wood resin are needed.

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