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*Tiina Sarja*

MEASUREMENT, NATURE  
AND REMOVAL OF STICKIES  
IN DEINKED PULP

FACULTY OF TECHNOLOGY,  
DEPARTMENT OF PROCESS AND ENVIRONMENTAL ENGINEERING,  
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*TIINA SARJA*

**MEASUREMENT, NATURE  
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Supervised by  
Professor Jouko Niinimäki

Reviewed by  
Doctor Hans-Joachim Putz  
Doctor Jaana Sjöström

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Faculty of Technology, University of Oulu, P.O.Box 4000, FI-90014 University of Oulu, Finland,  
Department of Process and Environmental Engineering, University of Oulu, P.O.Box 4300, FI-90014 University of Oulu, Finland

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### ***Abstract***

Stickies refer to tacky contaminants in recovered paper, excluding wood extractives. Stickies originate from adhesives, ink binders and coating binders. Stickies able to pass a sieve of 100 or 150  $\mu\text{m}$  (depending on standard) are called micro stickies, whereas the particles retained on the screen are called macro stickies. Dissolved and colloidal stickies are called secondary stickies. There are standard methods for macro stickies, but a standard method measuring the total amount of stickies is lacking. Furthermore, the size distribution, and nature of stickies in the sense if they are free particles or agglomerated with some other substances, has not been previously known. The information on the removal of stickies in different unit operations was also not known very well except for macro stickies. The aim of this thesis was thus to develop an analysis method for the total amount of stickies, determine the size distribution and nature of stickies, and find ways to better remove stickies in the deinking process.

Extraction with tetrahydrofuran (THF) and High Pressure Liquid Chromatography (HPLC) with Size Exclusion Column (SEC) was used here to separate hydrophobic polymers (stickies) from the pulp suspension. An Evaporating solvent Light Scattering (ELS) detector was utilized to quantify the polymers after SEC. This analysis procedure was used in this thesis to measure stickies. Fractionation of pulp before the analysis was carried out if information of different-sized stickies was desired.

The majority of stickies are micro stickies. A significant, although lower, portion of stickies are macrostickies, especially in the beginning of the deinking process. The dissolved and colloidal phase was found to contain wood extractives, and only trace amounts of stickies.

Flotation is very effective in stickies removal. Ink and micro stickies were removed nearly equally in flotation, because they both are hydrophobic and are both in an optimal size range for removal in flotation. Ink measurements may be used for estimating the trends of stickies removal in flotation. The stickies removal in flotation may be enhanced by optimizing the pulper chemistry.

***Keywords:*** chemical analysis, deinked pulp, ELS, extraction, flotation, HPLC-SEC, pulper chemistry, stickies, wood extractives



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Oulu, April 25, 2007

Tiina Sarja





## List of original papers

This thesis is a summary of the following publications, referred to in the text with the corresponding Roman numerals. Some unpublished data is also included.

- I Sarja T, Zabihian M, Kourunen P & Niinimäki J (2004) New method for measuring potential secondary stickies in deinked pulp filtrates. *Water Science and Technology* 50(3): 207-215.
- II Sarja T, Zabihian M & Kourunen P (2003) Control of potential secondary stickies in deinked pulp. Proc. 2003 TAPPI Fall Technical Conference, Chicago, USA, October 26-30, 2003. Paper 22-2.
- III MacNeil D, Sarja T, Reunanen M, Xu C-L & Holmbom B (2006) Analysis of stickies in deinked pulp. Part I: Methods for extraction and analysis of stickies. *Professional papermaking* 2006(1): 10-14.
- IV Sarja T, MacNeil D, Messmer M, Reunanen M & Niinimäki J (2006) Analysis of stickies in deinked pulp. Part II: Distribution of stickies in deinked pulp. *Professional papermaking* 2006(1): 15-19.
- V Sarja T & MacNeil D (2006) Effect of neutral deinking on stickies. Proc. 12<sup>th</sup> PTS-CTP Deinking symposium, Leipzig, Germany, April 25-27, 2006. Paper 15.
- VI Sarja T, MacNeil D & Künzel U (2006) Addressing the nature of stickies in deinked pulp. Proc. 2006 TAPPI Engineering, Pulping and Environmental Conference, Atlanta, USA, November 5-8, 2006. Paper 8-2.
- VII Sarja T, MacNeil D, Huber P & Niinimäki J (2007) Removal of stickies in flotation. *Progress in paper recycling*, accepted 2007.

In Papers I-II and IV-VII, the present author designed the experiments, analyzed the results and wrote the manuscripts. In paper III, the present author designed the experiments and analyzed the results together with the first author.



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# 1 Introduction

## 1.1 Background

Generally, the term “stickies” refers to sticky material in the recovered paper, but excludes wood extractives. The most common sources of stickies are adhesives used in attaching labels, advertisements, CD’s and any other additional material in newspapers and magazines, for binding catalogues, for envelope sealings, stamps, and many more; the other sources of stickies are ink binders and coating binders, i.e. latexes (Putz 2000). Waxes used in carton for packaging are also a significant source in recycling of old corrugated containers (OCC). Substances classified as wood extractives may also include, in addition to actual wood resin, fatty acids from deinking aids or resin acids from rosin sizes.

Stickies are one of the biggest technical challenges in using recycled fiber in papermaking. Stickies cause product quality problems, such as holes and specks in paper, which may lead to higher paper rejection or to customer reclamations. Runnability problems, such as sheet breaks, occur both at the paper machine and at printing houses. It is common to have a build-up of black and sticky or gummy deposits on the drying cylinders or calenders. Doctoring the cylinders helps to some extent, but does not totally solve the problem. Down-time due to washing and cleaning is the consequence of the runnability problems.

All of these problems cause lost production time and higher costs for the papermaker. Varying estimations on the total costs of stickies have been reported. A rather old estimation from 1996 claimed that there were yearly costs of \$700 million due to stickies in USA (Friberg 1996). McHugh *et al.* (2001) estimated losses of \$218 million per year for the linerboard and corrugating industry due to downtime due to the use of OCC. Bajpai (2006) reported costs of €400 million in the USA. The main sources of the costs were furnish downgrades and paper machine downtime. It is very difficult to estimate the costs due to stickies, because it is not always certain if for example stickies were the cause of the break.

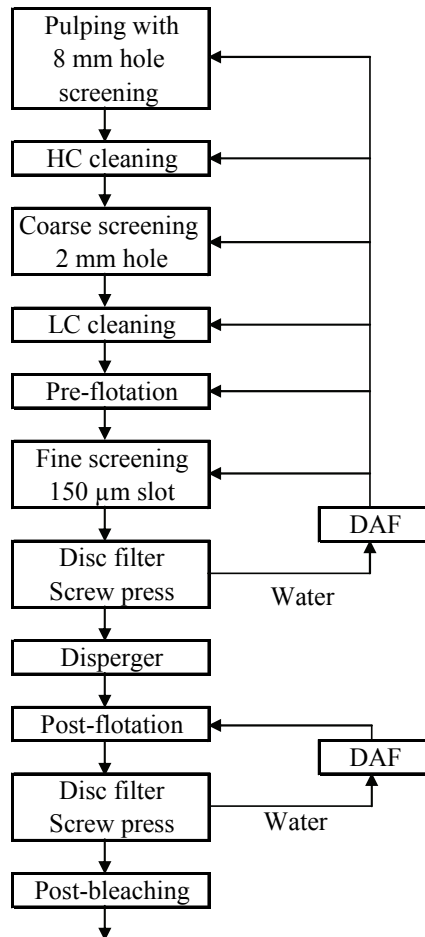
The lower price of deinked pulp (DIP) than mechanical pulp of corresponding quality has increased the use of deinked pulp in manufacturing of printing and writing papers. Newsprint grades in Europe are nowadays many times made from 100% recycled fiber. The recycling rate of paper has increased, and also the use of adhesives has increased steadily (Engert & Haveri 2004) leading to increasing amount of stickies in recycled fiber (Hamann 2005a). The

closure of water circuits also results in build-up of contaminants in the water loops. These facts have naturally decreased the paper quality and increased the problems related to stickies. However, constantly higher quality paper grades are made from recycled fiber.

Generally, stickies may be divided into macro, micro and secondary stickies. Macro stickies refer to tacky particles that retain on a laboratory screen of 100 or 150  $\mu\text{m}$  (Blanco *et al.* 2002; Doshi *et al.* 2003a; Hamann & Strauss 2002). The size comes from the usual slot size of fine screening. Stickies smaller than 100 or 150  $\mu\text{m}$ , but bigger than 1-5  $\mu\text{m}$  (Doshi *et al.* 2003a; Hamann & Strauss 2002) are called micro stickies. Dissolved and colloidal stickies smaller than micro stickies are called secondary or potential secondary stickies (Faul 2002; Hamann 2005a). The secondary stickies are thought to become harmful after changes in temperature, pH, or chemical environment (Blanco *et al.* 2002; Carré *et al.* 1998; Li & Zhan 2005).

### **1.1.1 Production line for deinked pulp**

A typical process diagram for production of deinked pulp for newsprint is depicted in Figure 1. The arrangement of the unit processes may vary significantly from mill to mill, and the amount of e.g. flotation cells or the arrangement of screening stages varies. Furthermore, all mills do not have the second loop at all, while some mills have even a third loop with additional washing or bleaching, if higher quality pulp is required.



**Fig. 1. A simplified process diagram of a typical deinking line for newsprint or supercalendered (SC) paper. DAF = dissolved air flotation, HC = high consistency, LC = low consistency.**

In pulping, the recovered paper is disintegrated into a pulp suspension, typically at 16-18% consistency, with the aid of warm water and chemicals. Low consistency slushing as low as 3% is also sometimes used. There, the ink and stickies are detached from the paper for the first time. Conventional alkaline pulping chemistry includes sodium hydroxide for swelling the fibers, hydrogen peroxide to prevent alkali yellowing, sodium silicate for e.g. stabilizing the peroxide and preventing re-deposition of ink on fibers, and soap or fatty acids in

Na-form to work as surfactants to detach ink from the paper, and in Ca-form to collect the ink particles for bigger and better floatable particles later in flotation. Synthetic surfactants may replace partly or totally the soap or fatty acid. When using synthetic surfactants, the amount of sodium hydroxide and peroxide and sometimes also sodium silicate may sometimes be reduced or totally left out, resulting in a lower pH.

A screening section with typically 7-8 mm holes is in the end of the pulper. There, the biggest contaminants, such as plastic, CD's and big adhesive tapes are removed. Coarse screening with 2 mm holes further removes the bigger contaminants including large stickies at a consistency of about 3-5%. In cleaning, depending on the operation mode, lighter or heavier substances than water are separated in hydrocyclones; these contaminants include mainly sand, glass, plastic and styrofoam particles. The density of adhesives is often very close to that of water, which makes the stickies removal in cleaners difficult. HC cleaning is typically carried out at 2-5% consistency and LC cleaning at 1%, respectively.

Flotation is the key process unit for removing ink and micro stickies. Air bubbles are fed to the pulp suspension at about 1%. The ink, stickies, and also some fillers and fibers rise with the bubbles to the foam, which is collected from the top. The removal efficiency of flotation is the best at the particle size range that ink has after it has been agglomerated into slightly bigger particles with a collector chemical (Ackermann *et al.* 2000). The hydrophobic character of ink is also the major reason why ink is so well removed in flotation.

Macro stickies are not so well removed in flotation, but are very well removed in fine screening at a consistency below 1.5% and with a slot size down to 0.12 mm. Other bigger contaminants, such as flakes of non-disintegrated paper or dirt specks, are also removed in fine screening. There are many possibilities to connect the screening stages, e.g. by feed-forward or cascade mode.

The deinking line is often split into two separate water loops to prevent contaminants from following the pulp through the process. The dewatering of pulp is typically carried out with a combination of a disc filter and a screw press. The water circuits flow according to the counter-current principle. Stickies may end up in the filtrates in dewatering and thus accumulate in the water loop if the water loops are closed and no clarification of water is carried out. The filtrates may be clarified with dissolved air flotation (DAF), and are used as dilution water in earlier process stages. In DAF, very small air bubbles are generated. Air is dissolved in water under pressure, and as the pressurized water is led to the



flotation cell, the pressure drop creates micro bubbles as the dissolved air becomes gaseous. The foam is collected at the surface of the DAF.

Dispersion of pulp may be carried out in the beginning of the second loop at 22-32% consistency in order to detach more ink for removal in post-flotation and to make residual dirt specks and stickies smaller. Post-flotation and dewatering follow the disperger. A post-bleaching stage may be carried out in the end of the deinking line with hydrogen peroxide or sodium dithionite, if a higher brightness is desired.

## 1.2 The research problem

The following problems in stickies control were identified:

1. **The lack of a measurement or analysis method for stickies determining the total amount of stickies.** There are standardized methods for measuring macro stickies, but not for micro stickies. There is a variety of different methods to detect stickies, but all methods measure slightly different things.
2. **The unknown nature of stickies.** Information about the size distribution and nature of stickies has been limited to macro stickies. The nature of stickies is important for control: The control strategy depends on if the stickies are loose or attached to something.
3. **Removal of stickies in the unit processes of a deinking mill.** Better removal of stickies is desired in order to reduce the problems. Removal of stickies in different unit operations has been well known only for macro stickies.

## 1.3 Hypotheses

The aim of this thesis was to find solutions to the above mentioned research problems. The following hypotheses were tested:

1. A method based on solvent extraction and HPLC-SEC (High Pressure Liquid Chromatography - Size Exclusion Column) to separate hydrophobic polymers followed by an ELS (Evaporating solvent Light Scattering) detector to quantify them is a viable way to measure stickies.
2. Stickies in deinking lines are mostly micro stickies, although macro stickies are also important. Dissolved and colloidal stickies, i.e. secondary stickies, do

not exist to any great extent; however wood extractives are found in dissolved and colloidal form in deinking waters.

3. Secondary stickies were earlier said to originate from dissolved and colloidal stickies due to changes in pH, temperature, charge, etc. leading to agglomeration. The changes in process conditions are also known to cause deposit problems on the paper machine, and the agglomeration of secondary stickies have been suspected to be the reason. Deposition due to process changes is not due to secondary stickies, as there are no dissolved and colloidal stickies, but due to dissolved and colloidal wood extractives, or micro stickies.
4. Ink and micro stickies are removed by the same mechanism in flotation, as they are both hydrophobic and have a similar size distribution. They may, furthermore, agglomerate with each other.
5. The stickies removal in flotation may be enhanced by changing the pulper chemistry.

#### **1.4 Research assumptions**

This research deals with deinked pulps made of mixtures of old newspaper (ONP) and old magazines (OMG) used for production of newspaper, supercalendered (SC) paper and other printing and writing papers. Processing of office waste and old corrugated containers (OCC) for production of tissue or board is not discussed in this thesis, although some examples are sometimes presented.

## 2 Measurement of stickies

Many different ways to measure stickies are found in literature. They may be divided into methods that measure the quantity, chemical composition or deposition tendency of pulp. The methods measuring the quantity of stickies include e.g. solvent extraction methods, macro stickies methods based on screening and image analysis, chemical analyses, and miscellaneous other methods for micro and secondary stickies. The methods measuring the deposition tendency include wet and dry deposition tests and tackiness testing of stickies.

### 2.1 Quantity and chemical composition of stickies

#### 2.1.1 Solvent extraction methods

Extraction with an organic solvent is commonly used to separate hydrophobic substances from the pulp, water or deposit sample. The extraction may be carried out with different extraction techniques, such as reflux, soxhlet (or similar automated versions, e.g. soxhtech and soxhtherm), accelerated solvent extraction (ASE), supercritical fluid extraction (SFE), solid phase extraction (SPE) or simply extracting the sample in a test tube, perhaps with the aid of ultrasound.

Gravimetric extraction uses only the weight of the substances soluble in the solvent used: The extract is dried and weighed. The gravimetric determination of extract is easy to carry out, but does not tell anything about the content of the extract. The result is, furthermore, very dependent on the solvent used. None of the solvents dissolve all of the stickies present in the pulp, and always non-stickies are also included in the result. There are differences in the solubilities of the stickies in different solvents.

Dichloromethane (DCM) is very commonly used in extracting stickies (Delagoutte *et al.* 2001; Dionne *et al.* 2006; Gruber *et al.* 2000; Johansson *et al.* 2003; Philippaerts 2000; Ward *et al.* 1994). It is a natural choice, because DCM is often used as a solvent in the adhesive solutions before they are applied (Warwick 2005). Dimethyl formamide (DMF) was used by Hamann (2005b) and chloroform by Ben *et al.* (2004) and Huo *et al.* (2001). Ben *et al.* found a poor dissolution of stickies in the chloroform. Trichloroethane (TCE) was earlier used for analysing wax, but later on the production of TCE was stopped due to its toxicity (Cao & Heise 2001). MTBE (Methyl-tert-butyl-ether) is used in

analysing wood extractives by liquid-liquid extraction (Örså & Holmbom 1994; Lenes *et al.* 2001). Acetone with the addition of phosphate has also been used for extracting DIP water (Lenes *et al.* 2001). Tetrahydrofuran (THF) has been used for quite a long time (Sjöström 1987; Asp 1994; Holmbom 1997). Asp tested the solubility of different adhesives in THF, and found that most adhesives tested were partially or totally soluble.

Comparisons of solvents have been reported only a few times. Hamann (2005b) found that DMF gives higher gravimetric values than DCM. Cao & Heise (2001) made a comparison of solvents for extracting wax from OCC: Methyl ethyl ketone (MEK), hexane, acetone and TCE gave approximately the same gravimetric amount. FTIR also gave similar spectra: Only paraffin was not dissolved in acetone. Blaney & Hossain (1997) used different solvents for detecting stickies. Ethanol-benzene gave the highest amount of gravimetric extract, and acetone, DCM and hexane slightly lower values.

Solvent extraction was chosen to be the basis of the stickies measurement method, as it takes into account stickies of all sizes, and afterwards analytical instruments can be used for analysis of the extract. It was impossible to select the best solvent based on the information in the literature. Consequently, three most promising solvents, DCM, DMF and THF, were compared in Paper III. The ideal solvent would dissolve all stickies and only stickies, especially if it was to be used in gravimetric determination of extractable material.

The stickies content of the extracts was analyzed by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). THF and DCM were found to be almost equally good in extracting stickies. DMF extracted slightly more stickies, but dissolved also lignin, which resulted in much higher gravimetric values. THF was selected for further use because of its easy handling compared to DMF and due to DCM being banned for health reasons in some of the laboratories where the method was going to be adapted. Details of the solvent selection are discussed in another thesis by the first author of Paper III.

Sequential extraction with different solvents overcomes the problem of not all stickies dissolving in one solvent. Lee & Kim (2006) used ethanol, hexane and chloroform to have better yield in the analysing the gravimetric amount of extract. However, it makes the analysis far more labor intensive.

### **2.1.2 Chemical analyses**

The amount of different adhesives and other stickies compounds in pulp suspension or in deposits may be analyzed with various analytical techniques. While it is not the purpose here to review in detail their operating principles, instead applications have been searched in literature.

Fourier Transform Infra Red spectroscopy (FTIR) is commonly used to identify organic and inorganic substances. It is sensitive to functional groups; the wavelength of light absorbed is characteristic of the chemical bond. FTIR is commonly used in identification of sticky substances (Allen & Ouellet 2006; Cao & Heise 2001; Delagoutte *et al.* 2001; Guo & Douek 1995; Nelson *et al.* 1997; Ward *et al.* 1994; Yordan & Maat 1997). Johansson *et al.* (2003) were able to quantify stickies with IR (Infrared spectroscopy) analysis and multivariate data analysis of the spectra.

Gas Chromatography (GC) combined with Mass Spectrometry (MS) can detect and quantify volatile components, and it is used for quantifying wood extractives (Guo & Douek 1995; Örså & Holmbom 1994). The separation of different compounds in gas chromatography takes place in long columns depending on the chemical and physical properties of the substances. The compounds emerging from the column are then detected by MS. For analysing stickies, a pyrolysis unit is needed before GC/MS. In pyrolysis, stickies are decomposed into volatile compounds in a helium atmosphere and high temperature. The pyrolysis products are then identified or quantified. Py-GC/MS has been used by many authors (Holmbom 1997; Kanto Öqvist *et al.* 2005; Lenes *et al.* 2001; Odermatt *et al.* 1998, 1999, 2005a-b; Sjöström *et al.* 1987; Sjöström *et al.* 2004) in analysing stickies and other paper additives in pulp, deposit and paper. Py-GC/MS was also used in this thesis to quantify individual stickies compounds.

Thermogravimetric Analysis (TGA) is based on the fact that the pyrolysis temperature of many synthetic polymers in a nitrogen atmosphere is higher than that of natural polymers (i.e. cellulose, lignin and hemicelluloses in wood fibers). The method may be used without extraction as a pre-treatment: The weight loss of the dried sample is measured as a function of temperature. A weight loss between certain temperatures may be used for calculating the amount of synthetic polymers (stickies). However, in this method, the long fibers need to be screened out before the measurement in order to increase the accuracy and precision of the method, as fiber material partly pyrolyzes in the same temperature as stickies.

Because of that, macro stickies are not included in the result (Castro *et al.* 2001; Guo & Douek 1995).

In High Pressure Liquid Chromatography (HPLC), the substances are separated in the liquid phase. Sjöström *et al.* (1987) used HPLC for separating stickies from other substances with a Size Exclusion Column (SEC), where substances are separated based on molecular size. They used IR and Py-GC/MS for the polymeric fraction and GC for the low molecular size fractions. Holmbom (1997) also used the separation of polymers from other hydrophobic substances with HPLC-SEC and quantification of polymers with Py-GC/MS.

HPLC-SEC was selected to separate polymeric material (stickies) from wood extractives and other non-stickies material in the THF-extract. Quantification of polymers was still required. IR is usually used only for identification of substances, and quantification would require multivariate data analysis (Johansson *et al.* 2003). Py-GC/MS was used even in quantification, and it was shown to give good results. However, it is quite laborious, so a faster method was desired for use in routine analysis. Different detectors may be used after HPLC-SEC. In Paper III, an Evaporating solvent Light Scattering (ELS) detector was applied after HPLC-SEC to quantify the polymers. An ELS detector is a universal detector, which detects and quantifies all material except for very small and highly volatile molecules. The downside of the detector is that there is no direct identification of individual compounds, and they must first be separated in a chromatographic column. The response factors are almost identical for the substances involved in this study, which makes the quantification reliable with ELS. Details of this matter are discussed in another thesis by the first author of Paper III. The HPLC-SEC system presented in Paper III proved to be reliable and fast for use in routine analyses, and Py-GC/MS was used when information about the individual components was needed.

A refractive index detector could not be used. It is universal, but it has poor sensitivity and different substances have different response factors making the quantification difficult. Neither could an ultra violet (UV) detector be used, because not all stickies absorb UV light, and the background absorption from the solvent was too high.

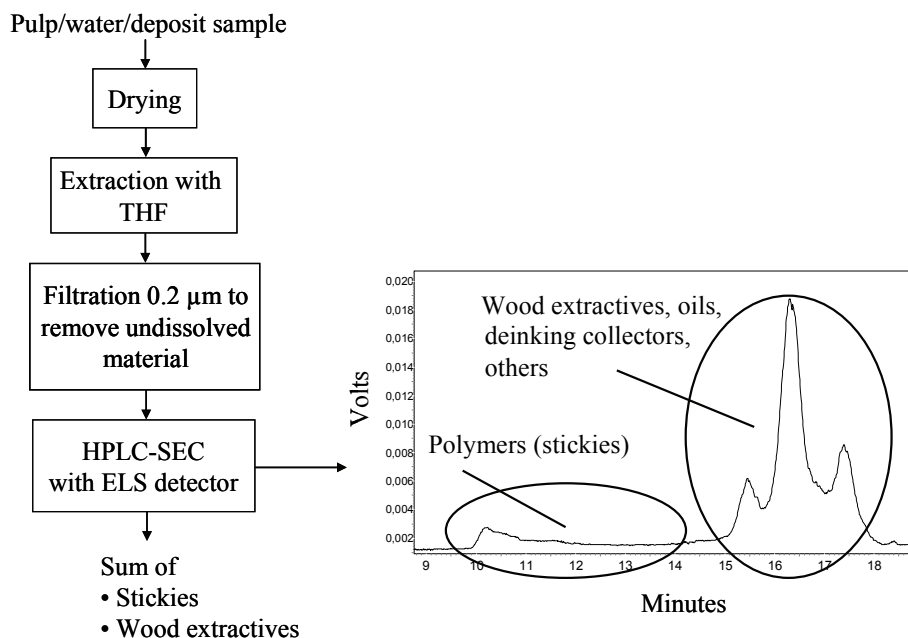
Other techniques are also possible to use, such as Nuclear Magnetic Resonance spectroscopy (NMR) (Guo & Douek 1995), but not much data on that is available.

Very complicated schemes to analyze deposits have been published by Guo & Douek (1995) and Wilken & Strauss (1984) with sequential extraction and

different analytical devices. These schemes are not, however, very convenient for regular use as they are very laborious and require many analytical instruments.

The stickies analysis method shown in Fig. 2 was used in Papers III-VII. In the method, the deposit, pulp, or water sample is freeze-dried, and extracted with THF. The extract is filtered through 0.2  $\mu\text{m}$  filter made of PTFE (polytetrafluoroethylene) to remove any undissolved substances, and analyzed by HPLC-SEC and ELS detector. The calibration was done with triglyceride or polystyrene in THF. As the separation of polymeric material from wood extractives was not perfect in SEC, an integration technique seen in Fig. 2 was used. This division between polymers and wood extractives was confirmed by Py-GC/MS results (Paper III).

The THF-soluble polymers quantified with this method are defined as stickies in this thesis. In Paper IV, where the same samples were analysed with both HPLC-SEC and Py-GC/MS, the polymers analysed with HPLC-SEC were called “polymers” and the polymers analysed with Py-GC/MS were called “stickies”, respectively.



**Fig. 2. The stickies analysis method (Paper III). THF = tetrahydrofuran, HPLC-SEC = High Pressure Liquid Chromatography - Size Exclusion Column, ELS detector = Evaporating solvent Light Scattering detector.**

### **2.1.3 Measurement methods for macro stickies**

There are three standardized macro stickies measurement methods: TAPPI method T277 (TAPPI 1999), INGEDE (International Association of the Deinking Industry) method no. 4, and a method by the International Organization for Standardization (ISO) based on screening and either visual inspection (ISO 15360-1:2000) or image analysis (ISO 15360-2:2001). These or slightly different methods are widely used in the industry and research.

Most of the laboratory methods that measure the amount of macro stickies are based on either handsheet making (McHugh *et al.* 2001) or screening of the pulp through 100 or 150  $\mu\text{m}$  slots (INGEDE Method 4, ISO 15360 1-2; Johansson *et al.* 2003; TAPPI 1999; Delagoutte & Laurent 2002). The pick-up of screen rejects with plastic is also used (Lee & Kim 2006). These pre-treatments are followed by dyeing the stickies, the background, or both to have a greater contrast between the background and stickies. The stickies are then quantified as area ( $\text{mm}^2/\text{kg}$ ) or in number of stickies per kg of dry pulp. Errors of 10-20% have to be accepted in macro stickies measurements (Schabel 2000).

Johansson *et al.* (2003) found a good correlation between the macro stickies analyzed by image analysis and screen rejects analyzed with DCM extraction and quantification of stickies with FTIR. Hsu *et al.* (1997) analyzed the macro stickies in the screen residue to most often be polyacrylates.

Allen & Ouellet (2006) reported that macro stickies measurement did not correlate with the deposit problem on the paper machine.

The macro stickies measurement methods are not discussed here in more detail, because they were not used in this thesis.

### **2.1.4 Measurement methods for micro and secondary stickies**

The extraction methods – with or without more detailed analysis with analytical instruments – determine the amount of materials of all sizes soluble in that solvent. Fractionation of pulp before analysis may be used to separate micro stickies from macro stickies in the pulp. Johansson *et al.* (2003) used a laboratory Somerville screen with 0.15 mm slots and a Dynamic Drainage Jar (DDJ) with a hole size of 76 and 20  $\mu\text{m}$ . Huo *et al.* (2001) also used fractionation of pulp with a DDJ by using a 200 mesh (76  $\mu\text{m}$ ) wire, followed by filtering the fines suspension before extraction of the fines fractions. It is clear that if the division between micro and macro stickies is based on screening or filtration with DDJ, the



separation is not perfect. That means that micro stickies include stickies larger than the opening, and on the other hand, not all micro stickies necessarily go through the screen. DDJ filtration and centrifugation before stickies analysis was used in Papers IV-VI to separate different-sized stickies.

Besides extraction, there is a variety of other ways to measure the amount of micro stickies. De Jong *et al.* (2006) suggested a measurement method for micro stickies from OCC to be made by collecting the screenate (fraction passing the screen) of the screening when making TAPPI T277 macro stickies measurement. The screenate is stored in refrigerator for two weeks, and the macro stickies measurement is then done to the screenate. This method is maybe not suitable for ONP/OMG systems due to the smaller amount of stickies than what is found in OCC.

The “Pitch-Counter” method detects the amount of hydrophobic particles in a fines suspension. The hydrophobic particles are dyed with a fluorescent dye and counted under a fluorescent light (Hamann *et al.* 2004; Künzel & Prinz 2006) or with automatic laser counter (Yu *et al.* 2003). The advantage of the pitch-counter is that not only free hydrophobic particles are seen but also e.g. fines particles where a hydrophobic particle is attached. Hemacytometer, where pitch is counted by hand under light microscope, is commonly used for pitch counting. It was used by Huo (2002) to evaluate the stability of model micro stickies.

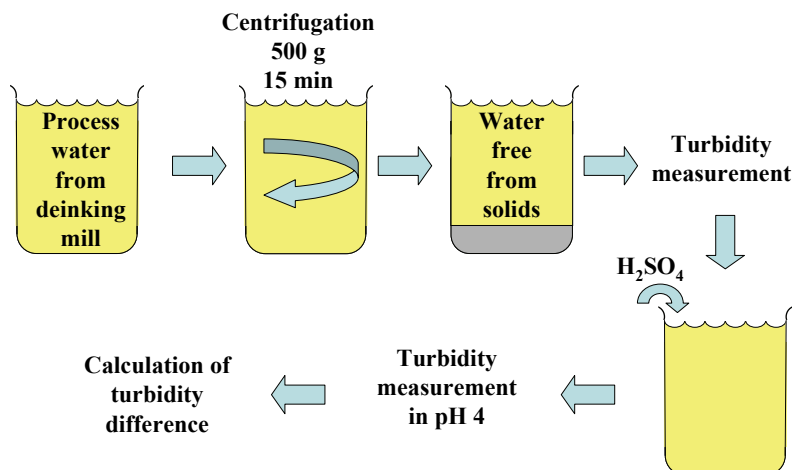
A method similar to the pitch counter is flow cytometry (FCM) used by Vähäsalo (2005). The device is adopted from medicine. In this method, the pulp is also filtered with a DDJ to obtain a fines-suspension. The stickies are stained with fluorescent dyes and light scattering and fluorescence of individual particles is measured as the particles pass a focused laser light.

Total organic carbon (TOC) content between 5 kDa and 25  $\mu\text{m}$  was introduced as a way to measure micro stickies (Haynes 2003). The drawback of the method is that other substances than stickies also contribute to TOC.

Turbidity may be used to measure the amount of colloidal particles in water phase. Approximately 45% of the turbidity-inducing particles come within the size range of 5-40  $\mu\text{m}$  (Berger 2002).

A simple way to measure contaminants in the water phase was needed to study the performance of dissolved air flotation. A measurement method based on turbidity measurements at two pH values was used in Papers I and II. The idea was to make dissolved and colloidal substances more visible with a pH shock. Those substances were then called potential secondary stickies. The method is depicted in Fig. 3. The water sample is centrifuged before the turbidity

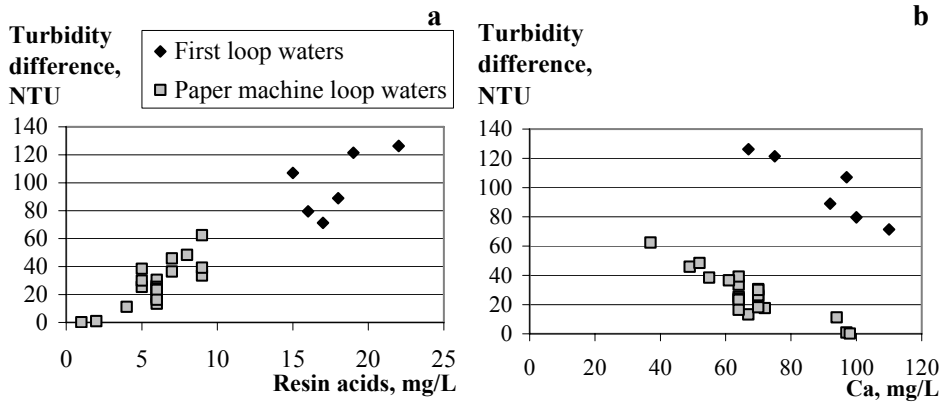
measurement, as turbidity of non-centrifuged water measures mainly the suspended solids. The pH of the centrifuged water is lowered to 4, and the turbidity is measured again.



**Fig. 3. The turbidity difference method used in Papers I-II.**

The turbidity difference method was found to correlate well with the wood extractives content, and even better with resin acids (Fig. 4a). In the pH shock, the fatty and resin acids become colloidal from their previous dissolved state and thus become visible as measured by turbidity. Later, the centrifuged water fraction of deinked pulp was found to contain only wood extractives, as only trace amounts of stickies were found (Paper IV). Thus, potential secondary stickies actually refer to dissolved and colloidal wood extractives, which are not considered as stickies. This is discussed more in Chapter 3.3.3. The correlation seen in Fig. 4a supports the hypothesis that the change in pH agglomerates the wood extractives in the deinked pulp water phase: i.e. the origin of secondary stickies would be wood extractives.

The negative correlation of the turbidity difference with calcium (Fig. 4b) is due to the dissolution of calcium carbonate under pH 6.5.



**Fig. 4. The correlation between turbidity difference and (a) resin acids and (b) calcium (Paper I). NTU = Nephelometric Turbidity Unit.**

## 2.2 Deposition tendency

The deposition methods aim at imitating the real deposition phenomena occurring in the wet or dry sections of the paper machine. The deposition test methods may be divided in three main categories: Methods measuring deposition tendency in wet conditions, methods measuring deposition in the dry end of paper machine, and methods measuring the tackiness of stickies.

Wet deposition testers are more commonly found in the literature than dry deposition testers, even though in modern mills, nowadays, deposition in the wet end of a paper machine is reported more rarely than deposition in the drying section. In wet deposition testers, pulps are allowed (or even encouraged) to form deposits on various substrates, e.g. plastic (Blanco *et al.* 2002; Doshi *et al.* 1997; *et al.* 2002; Sitholé *et al.* 1997), metal (Welkener *et al.* 1993; Kanto Öqvist *et al.* 2005), paper machine wire (Carré *et al.* 1998; Gruber *et al.* 2000; Lee & Kim 2006; Putz *et al.* 2003), etc. sometimes with the help of cationic polymers to cause destabilization of the secondary stickies (Carré *et al.* 1998; INGEDE Method 6). Vähäsalo (2005) pressed the pulp in a nip to simulate the press section of a paper machine. The amount of deposition is determined by extraction, surface weighing or by image analysis. Usually the tests are performed in laboratory, but sometimes deposition substrates are immersed in the process (Kanto Öqvist *et al.* 2005).

Deposition tests simulating the dry end of a paper machine are much more rarely reported. One was used by Fike *et al.* (2006) where a sheet was made to contact a heated curved metal coupon under pressure. Then the stickies, either in the sheet or in the metal coupon, were stained or calculated under microscope.

Another dry end deposition method is described in INGEDE Method 9. Paper sheets are dried against a chromium plated metal plate in a drying cabinet of 93°C for 8-10 minutes. The stickies adsorbed on the plate are dyed with a fluorescent colorant and counted with a microscope under ultraviolet light.

A deposition test imitating the dry end was reported by Delagoutte *et al.* (2001). A total of 20 handsheets are dried against a sheet of aluminum foil at 104°C for six minutes. The stickies deposited on the aluminum foil are then quantified gravimetrically by extraction with DCM. FTIR analysis on the extract ensures that the contents are actually stickies.

The deposition test method developed by Delagoutte *et al.* (2001) was used in Paper V with some modifications. Handsheets were made in a Büchner funnel with a 1% pulp suspension from a screened pulp. For deposition, a 10 cm × 10 cm sheet of aluminum foil was placed on a heater kept at 100°C. A handsheet was placed on the foil under a weight for two minutes. The foil was removed, and stickies on it were analyzed with the analysis method shown in Fig. 2 (THF-extraction + HPLC-SEC), whereas Delagoutte *et al.* (2001) used gravimetric amount of extractable material. There are large variations in the amounts of deposition on the foil, and therefore the values are reported as averages of several foils.

Tack methods are also used to determine the tackiness of stickies. Fike & Banerjee (2004) used a “Polyken probe tack” measurement on adhesive films. Vähäsalo (2005) measured tack with a probe that was pressed against a latex film with a known stress. The probe was then retracted until it was released, and the strain was measured. The relation of stress and strain was then the measure of tackiness.

Putz & Hamann (2003) compared different deposition methods, but did not find any of them to be applicable in all cases. They suggest selecting the measurement method for each problem area separately.

## 2.3 Summary of the methods

The stickies measurement methods presented in this chapter are based on different principles. Because of that, they also tell about different things making the comparison of the results very difficult.

Doshi *et al.* (2003a-b) made a comparison of different microstickies measurement methods. A stickies-rich pulp and a totally stickies-free pulp were mixed in different portions and micro stickies were detected. Some of the deposition methods were successful in showing the trend, while some of the methods did not detect the differences between the pulp mixtures. However, it was suspected that there was not very much micro stickies, but mainly macro stickies in the stickies-rich pulp to start with.

Table 1 below summarizes the main positive and negative sides of the most common stickies measurement method classes.

**Table 1. Summary of the most common stickies measurement method classes and their main positive and negative features.**

Method class	What does it measure?	Main positive features	Main negative features
Macro stickies methods	Sticky particles retaining on a 100 or 150 $\mu\text{m}$ slotted screen	Standardized methods, widely in use	Ignore micro stickies
Gravimetric solvent extraction	The amount of substances soluble in the solvent used	Stickies of all sizes included	Also non-stickies included in the analysis; solvent-dependent results
Solvent extraction + analytical quantification of sticky substances	The substances / substance class identified with the detector	Quantified substances of all sizes included, non-stickies not included in the result	Does not describe the tackiness; requires expensive instrumentation
Wet deposition testers	Amount of depositing material in wet conditions	Imitates real deposition phenomena	Deposits in the drying section more common than in the wet end; large variations in the results
Dry deposition testers	Amount of depositing material in drying section conditions	Imitates real deposition phenomena	Large variations in the results

A common negative side of all stickies methods is that their correlations with the runnability problems of the paper machine have not been proven. Another common drawback is that none of the methods measure all of the stickies and

only stickies. The closest methods to that ideal case are the sequential extraction procedures that utilize many analytical instruments.

Zellcheming (2006) recommends testing methods for micro stickies to detect at least one of the characteristics number, size or weight and at least one of the characteristics adhesion/tackiness or surface energy. Solvent extraction techniques do not, however, detect adhesion, tackiness or surface energy.

### **3 Nature of stickies and wood extractives in deinked pulp**

The origin, amount, size, and the distribution of different-sized stickies in deinked pulp are discussed in this chapter. The attachment of stickies to other substances is also discussed.

#### **3.1 Classification of stickies**

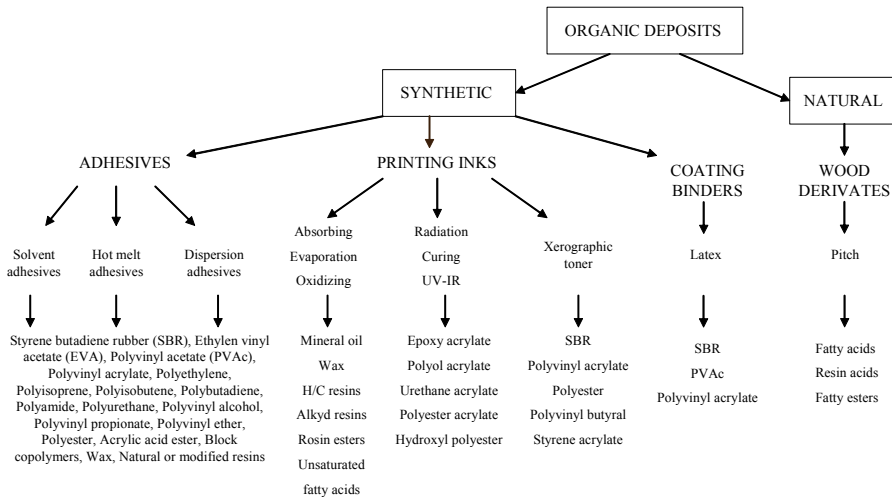
Various authors (e.g. Blanco *et al.* 2002; Doshi *et al.* 1997; Delagoutte *et al.* 2001; Hamann & Strauss 2002; Hanecker 2000; Huo *et al.* 2001; Pawlowska & Ryan 1999; Putz 2000; Zellcheming 2006) have defined stickies retaining on a 100 or 150  $\mu\text{m}$  screen as macro stickies, and stickies passing the screen as micro stickies. There is no upper limit for macro stickies, but stickies up to 2 cm in diameter have been sometimes detected after coarse screening (Kaltenegger 2006). The dissolved and colloidal stickies smaller than 1-5  $\mu\text{m}$  are called secondary stickies, or potential secondary stickies (Doshi *et al.* 2003a; Faul 2002; Hamann 2005a; Hamann & Strauss 2002; Zellcheming 2006). This division is widely accepted in industry and research.

Secondary stickies are said to be composed of dissolved and colloidal components of various materials, and agglomerate during sudden changes in the wet end chemistry or process conditions which result in the destabilization of the dissolved and colloidal materials which then deposit (Carré *et al.* 1998; Blanco *et al.* 2002; Faul 2002; Li & Zhan 2005; Philippaerts 2000). The latter part of the statement is true without a doubt, as papermakers have many times seen that the temperature, charge or pH shocks cause an outbreak of stickies deposits. However, according to the results in Chapter 3.3.3, the origin of the deposits formed due to those changes is not dissolved and colloidal stickies, but most likely micro stickies.

Faul (2002) concluded that stickies can both fragment into smaller particles (from macro to micro and further on to secondary stickies) and aggregate back from secondary stickies to micro stickies and even to macro stickies. However, evidence of this on mill scale is not available in literature.

### 3.2 Synthetic polymers

A frequently cited figure of the substances causing organic deposits is seen in Fig. 5 below.



**Fig. 5. Contaminants frequently identified in paper machine deposits from recovered paper processing mills (Putz 2000).**

In Fig. 5, the origin of organic deposits is divided into four main categories: Adhesives, printing inks, coating binders and wood extractives. The adhesives are usually, furthermore, divided into pressure sensitive adhesives (PSA) and hot melt adhesives (HMA). PSA's are tacky at all temperatures and HMA's are applied molten to the substrates, and as the HMA cools down, it adheres to the substrate. PSA's contain polybutadiene, polyisoprene, copolymers of styrene, with butadiene or isoprene, polyacrylates, and copolymers of vinyl acetates and acrylates. The most common acrylic monomer used is 2-ethylhexyl acrylate, which provides the polymer with a low glass transition temperature (Lyche *et al.* 1998). Many latex coatings are copolymers of styrene and butadiene, or vinyl acetates and acrylates. Some of the hot melt adhesives are made of ethylene and vinyl acetate copolymer (Lyche *et al.* 1998).

Fig. 5 shows that the most common stickies substances (excluding wood extractives) are polyacrylates, polyvinyl acetate (PVAc), ethylene vinyl acetates (EVA) and styrene compounds. These substances may be originated from several



sources, and tracking their origin, after they are found in the deposit, is very difficult.

The glass transition temperature ( $T_g$ ) is the temperature, where the adhesive transforms from a soft material into a hard substance (Tod 2005). The  $T_g$  of PVAc and EVA is 25-28°C (Packham 2005). The  $T_g$  of acrylates varies more depending on the application. In general, PSA's are rubbery at room temperature (Tod 2005). However, using  $T_g$  is not that straight-forward, because the substances in pulp suspension alter the  $T_g$  of an adhesive. If a polymer absorbs moisture, the material may plasticize resulting in a lower  $T_g$  (Tod 2005). Furthermore, some adhesives may become totally non-tacky in a water suspension. In the drying section, where the water evaporates,  $T_g$  may, in principle, be again applied. However, if fillers adsorb onto an adhesive particle, the  $T_g$  changes. Also, the temperatures in the drying section are well above the  $T_g$  of the common adhesive polymers.

It is quite unclear in which state the adhesives are while in the pulp suspension after the pulping. Huo (2002) noticed model micro stickies to have an electrical double layer, but the problem with model stickies studies is that it is not known how realistic those model systems are. Huo (2002) also measured model micro stickies to have a slight negative charge (-18  $\mu\text{eq/g}$ ). However, stickies were noticed not to affect the zeta potential or charge of the pulp in another study (Brouillette *et al.* 2005).

### **3.3 Stickies in pulp and deposits**

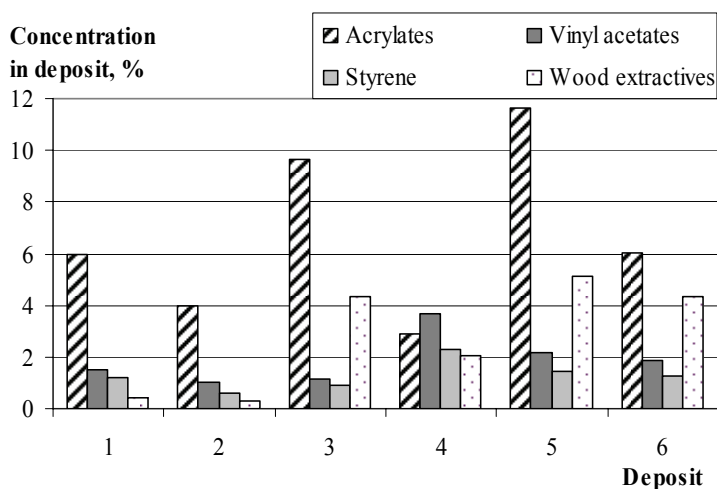
Data from various mills about the amount and state of stickies in pulp and deposits were collected, and they were compared to the values available in the literature. They are discussed in the following chapters.

#### **3.3.1 Composition of deposits**

It is very important to first analyze the deposits to find out what substances cause the deposition problem. Usually, almost all papermaking components are found in the deposits, but the key is to compare the headbox or final DIP furnish concentration of the suspected deposit-causing substances to the amount of the same substance in the deposit. If clearly more of the substance is found in the deposit than in the headbox furnish, the component might be the cause of the deposition.

Some information is available in literature on the composition of deposits. The deposits analyzed are, however, collected from different locations and analyzed with varying methods making the comparison difficult. Johansson *et al.* (2003) analyzed deposits which were found to contain 20-40% of DCM-extractable material. Filler material was also present in significant amounts. PVAc, acrylates and butadienes were detected to be the most harmful of the stickies substances. Guo & Douek (1995) found forming section deposits to contain fillers, resin and fatty acids, polyvinyl acetate, acrylates, EVA and SBR copolymer. Sjöström *et al.* (1987) found EVA, SBS, acrylic polymers and wood extractives in wire deposits. Allen & Ouellet (2006) analyzed wood resin and its metal soaps and stickies in a deposit from calender rolls of a newsprint paper machine using TMP (thermo mechanical pulp) and DIP.

It was important to determine what substances are the most harmful in forming deposits in the drying section in order to correctly focus the control strategies. Fig. 6 shows the amount of acrylates, vinyl acetates and styrene analyzed with THF extraction and pyrolysis-GC/MS, and wood extractives by HPLC-SEC or GC/MS from deposits from drying sections of six different paper machines producing newsprint or SC paper.



**Fig. 6.** Amount of stickies and wood extractives in deposits from six different paper machines (unpublished data).

Acrylate was the most abundant stickies monomer in five of the six deposits analyzed (Fig. 6). The proportional amount of acrylate was noticed to increase from the final DIP to the deposit (Paper IV). That means that it is not the poor removal of acrylate but its higher deposit potential that makes it often found as the cause of the deposit. Styrene, which had the highest concentration of stickies substances in the final DIP, did not have the highest concentration in the deposit. Polymers containing styrene are thus not removed as efficiently, but do not deposit as much.

Wood extractives had in every deposit lower concentration than the sum of polymers. Wood extractives might, however, be a significant contributor in the deposit formation. The other possibility is that stickies and wood extractives are in the same agglomerate, which then melts in the drying section. The main part of the deposits is, however, other material than stickies, mainly fillers and fiber material, and various other substances in smaller quantities.

### 3.3.2 Amount of stickies in pulp

Data from literature about the amount of all stickies in pulp after pulper and in final DIP were collected in Table 2. The raw material compositions were available only in three cases so that is why they are not listed here.

**Table 2. The amount of stickies after pulper and in final DIP; information from the literature with varying measurement methods.**

Pulper %	Final DIP %	Measurement method	Reference
0.5-2	-	Calculated from adhesive and paper production	Blanco <i>et al.</i> 2002
<4	-	Thermogravimetry	Castro <i>et al.</i> 2001
3.4	1.1	Gravimetric DMF-extraction	Hamann 2005a-b
0.18-0.3	-	Gravimetric DMF-extraction	Ward <i>et al.</i> 1994
1.4	0.45	Gravimetric DCM-extraction	Delagoutte & Brun 2005
0.7-1.2	0.15-0.25	Gravimetric DCM-extraction	Perrin & Julien-Saint-Amand 2006
0.2	0.05	DCM-extraction + FTIR	Johansson <i>et al.</i> 2003
0.1-0.2	0.03	THF-extraction + pyrolysis-GC/MS	Holmbom 1997
0.2-0.8	0.02-0.13	THF-extraction + HPLC-SEC	Table 3

Table 2 shows that varying concentrations of stickies have been determined due to the different measurement methods, raw materials, and seasonal variation. However, the results do not vary so much if methods more sophisticated than only gravimetric solvent extraction are used (three last rows).

OMG has higher stickies content than ONP (Røring *et al.* 2006; Lee & Kim 2006), which means that changing raw material affects the stickies concentrations of the pulp. However, regional differences might be so big that globally it is impossible to draw the conclusion that higher OMG content means always higher stickies content (see Table 3).

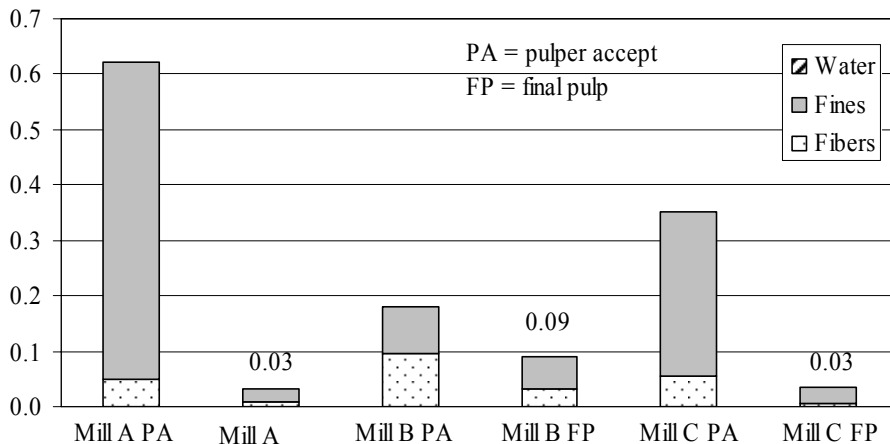
Seasonal changes have not been reported much, but Cao *et al.* (2003) concluded that there are seasonal changes in the macro stickies content in mills, but every mill has its peaks and valleys in different times. Lee & Kim (2006) also reported that there are large variations in recycled OCC stock.

### **3.3.3 Distribution of stickies in pulp**

Deinked pulp is a very heterogeneous suspension including fibers, fiber-fines, fillers, other fine material such as ink and stickies, other contaminants such as glass, plastic and sand and dissolved substances. The distribution of different-sized stickies in this mixture is important to know in order to focus the control of stickies on the right pulp fraction. The hypothesis that most of the stickies are micro stickies was tested. It was done in Paper IV by fractionating the pulp with Dynamic Drainage Jar (DDJ) by using a 200 mesh wire with 76 µm openings. The DDJ filtrate was centrifuged to separate the fine material from the dissolved and colloidal material. Also the hypothesis that the dissolved and colloidal fraction contains only wood extractives and only a minor amount of stickies was tested. In this way, the composition of secondary stickies was determined. Secondary stickies have been discussed in literature, but evidence on what they really are, is not available. Experimental data on only model secondary stickies have been reported.

Fig. 7 shows the distribution of stickies between fibers, fines (including fillers) and water phase (including only dissolved and colloidal substances) in the pulper accept and final pulps of three deinking mills.

**Stickies,  
g / 100 g dry  
pulp**



**Fig. 7. Distribution of stickies in deinked pulps from three mills (Paper IV).**

Fig. 7 shows that half or more of the stickies were found to be in the fines fraction and thus be micro stickies. In Paper VI, the fines fraction was further fractionated with a tighter screen (38  $\mu\text{m}$ ) and 98% of stickies in the fines fraction were found to pass the 38  $\mu\text{m}$  wire. In Paper V, the result of the fractionation was also that stickies are either very large or very small and pass the 38  $\mu\text{m}$  screen.

Similar results on the stickies being in fines have been determined by many authors with different measurement methods. Ward *et al.* (1994) reported that about half of the stickies after the pulper are washable and half are retained in the sheet during handsheet making. Allen & Ouellet (2006) found that poor dewatering of deinked pulp before the paper machine was one major cause of its runnability problems. That implies that micro stickies are also detrimental, and not just macro stickies. Delagoutte *et al.* (2001) found that most of the DCM extract is in the fine elements fraction containing mainly micro stickies. They also tested the different fractions with a dry end deposition tester, and found that the micro stickies were the main origin of the deposit potential, while macro stickies had a lower potential, and colloidal stickies a negligible contribution to the deposition. Ink has also been reported to be more abundant in fines (Lapierre *et al.* 2003). Bär *et al.* (2000) found that the majority of stickies in a laboratory pulp were micro stickies, and even smaller than 25  $\mu\text{m}$ . Odermatt *et al.* (2005a-b)

found that stickies are evenly distributed in the z-direction of paper, which means that stickies are smaller than the paper sheet (depending on the paper grade, but approximately 50  $\mu\text{m}$ ).

Stickies were not found in the centrifuged water fraction (Fig. 7). This result was verified by repeating the experiments with never-cooled pulp and also by analyzing the stickies with pyrolysis-GC/MS, by which only trace amounts of stickies were detected. Wood extractives, mainly fatty and resin acids, were found in the water phase. That is natural as they are in a dissolved form at alkaline pH's.

Although secondary stickies are very often mentioned to originate from dissolved and colloidal substances, almost no measurement data about dissolved and colloidal stickies exists. Johansson *et al.* (2003) concluded that only a minor amount of stickies is found in the dissolved or colloidal phase of the samples despite the fact that the major part of the stickies passed the 76  $\mu\text{m}$  screen when fractionated by DDJ. They determined that 2 to 5 mg/L stickies were in the colloidal or dissolved fraction. Some adhesives, e.g. polyvinyl acetate (PVAc) may become water soluble through hydrolysis and become polyvinyl alcohol. However, then it is no longer tacky. Internal water treatment by dissolved air flotation (DAF) can still remove stickies, because there is fine material and thus also micro stickies present in the filtrates to be treated by DAF's. One study by Hsu *et al.* (1997) is in slight contradiction with the results obtained here: They extracted recovered paper with water and analyzed the extract with FTIR. Usually they found only starch, but sometimes they found polymers made with carboxylic acid monomers, such as acrylic acid.

Based on these findings, secondary stickies should be redefined. If secondary stickies originate from dissolved and colloidal substances, then secondary stickies are actually wood extractives. In that case secondary stickies should be called something else, e.g. dissolved and colloidal substances. On the other hand, deposits due to pH, temperature, etc. shocks in the process could be originated from micro stickies or both dissolved and colloidal substances and micro stickies.

### **3.3.4 Free or attached**

Little research has been carried out to determine the nature of stickies, i.e. stickies being free particles or agglomerated with some other substances. The findings listed here are minor conclusions in the cited papers.

Doshi *et al.* (1997) found by microscoping artificial deposits produced in the laboratory that stickies contained fibers. Fike *et al.* (2006), on the other hand,

concluded that stickies and lignin would be attached, because stickies added to newsprint deposited easier on a metal plate than stickies added to bleached kraft pulp free of lignin.

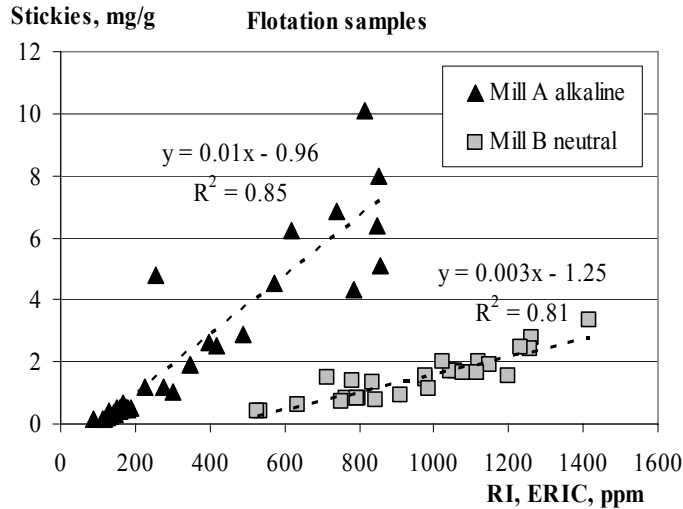
Fike *et al.* (2006) found that the stickies-fiber association is weak, and thus stickies are detached from their surface during pulping. Adhesives are also applied on coated paper, so stickies-filler-agglomerates might thus exist. Holmbom (1997) suspected that coating binders stay bound to fillers all along the deinking plant. In coated broke, the coating binders are not free but are together with other papermaking components (Vähäsalo 2005). Talc, and sometimes also calcium carbonate and kaolin, are used to detackify stickies (see Chapter 4.2.2). That means that fillers and stickies could exist as agglomerates. Enough information about the interactions between stickies and fillers is not available, but there is some hint of their possible co-agglomeration. Ash was measured in fractionation and flotation experiments in Papers VI-VII to clarify the issue.

Stickies and ash were noticed to behave similarly in the DDJ fractionation (Paper VI), but that was most likely due to them both being small enough to pass the DDJ wires. Flotation also sometimes removes stickies and ash in the same manner (Papers VI-VII), but the results are not consistent enough to be able to say that they were attached. Deposits almost always also contain both stickies and ash, which supports that they could be agglomerated. The amount of fillers in pulp is huge compared to the amount of stickies, and thus most of the fillers are stickies-free even if some attachment between them existed. That makes it hard to conclude whether they are attached or not. However, if stickies were totally covered with fillers, they would not be sticky anymore.

Deposits collected from the drying sections of paper machines are usually always black or a combination of black and gray; the black color is suspected to come from ink and the grey color from ink-contaminated fillers. Gonera *et al.* (2005) reported agglomeration of stickies and ink in the pulper. Bär *et al.* (2000) detected a correlation between brightness and stickies around flotation, which would indicate that stickies are attached either to ink, lignin or both, or that the particles lowering the brightness are removed in the flotation at the same rate as stickies. Sitholé *et al.* (1997) found that deposits in their deposition tester were black indicating that either the adhesives collect ink around them or that ink binders are more responsible for deposition than adhesives. The finding, that fresh newspapers form more deposits than old ones, supports the idea, too. Also Miller *et al.* (2004) found the deposits in a laboratory deposition tester to be black. The

dirt specks were, furthermore, found to include both stickies and inks (Fairbank *et al.* 2004).

The above mentioned studies imply that stickies and ink could be agglomerated. To verify this, ink and stickies results were collected from two mills. Figure 8 shows the results from two mills from the flotation feed and accept samples.



**Fig. 8. Stickies (mg/g of dry pulp) vs. ink in flotation feed and accept samples. Stickies were measured by THF-extraction and HPLC-SEC. RI (Residual Ink, measured at 700 nm) was used at Mill A and ERIC (Effective Residual Ink Concentration, measured at 950 nm) was used at Mill B (unpublished data).**

Fig. 8 shows that at each mill individually, the concentration of stickies and ink correlated when the feeds and accepts of the flotation were plotted. When data from all over the deinking plant was plotted, ink and stickies did not correlate. Because ink and stickies do not correlate elsewhere than in flotation, it seems that they are not attached, but that they have a similar tendency to be rejected in flotation due to their similar particle size distribution and surface properties. That may be true also in the case that part of the stickies would be agglomerated with ink, while others would not. For example, it seems logical that the ink binders stay black throughout the deinking process and are not washed away from the ink. One possibility is that ink and stickies are attached, but in macro stickies the stickies to ink ratio is higher than in micro stickies, because the specific surface



area of macro stickies is smaller than that of micro stickies. Then, for example in screening, far more stickies are rejected while most of the ink is passing the screen holes or slots. The different stickies to ink ratios would result in poor correlation between the concentrations of stickies and ink when all sample points are plotted in the same figure. Not enough data of ink over the screens is available to prove this.

The correlation between stickies and ink around flotation means that ink measurement could be used for the estimation of the amount of stickies in flotation samples, and thus the number of samples for stickies analysis may be reduced. When samples from other sampling points than the flotation feed or accept are added to the same graph, no correlation exists. Absolute values cannot be reported based on the ink measurements, but only trends. In laboratory flotations, higher correlation coefficients were obtained for a single flotation trial with several samplings over time. There, the correlations were extremely good for individual flotation laboratory tests.

There is no universal correlation between residual ink and stickies, but they correlate in a similar experimental flotation set-up. Here for example, Mills A and B had very different correlations. Overall, Mill B had lower amounts of stickies mainly due to the higher old newsprint content in the raw material used at the mill and due to a higher fresh water consumption.

### **3.4 Wood extractives**

Wood extractives or other fatty or resin acids in deinked pulp may originate from the recovered paper that was made from mechanical pulp, from the water connections if mechanical pulp is used in the paper machine, from the fatty acid or soap used in pulping and from rosin size used in the production of the recovered paper. Mainly fatty and resin acids were found in the deinked pulp or water loops (Papers I-II), and only very small amounts of neutral wood extractives; they are decomposed before the paper enters the deinking plant. The study was done at a deinking mill, whose pulp was used at a paper machine together with mechanical pulp resulting in a high probability of wood extractives being present in the water circuits of the deinking mill.

It is reported that paper mills using mixtures of TMP and DIP as raw material usually have more problems with sticky deposits than mills that use only TMP or DIP (Dechandt *et al.* 2004; Lenes *et al.* 2001; Allen 2002). That has also been shown with laboratory deposition testers, where a negative effect upon mixing

TMP and DIP mill waters has been noticed (Hanecker 2000; Lenes *et al.* 2001). Wood pitch has also been noticed to increase the white pitch deposition (Vähäsalo 2005). On the other hand, positive effects may also follow. Johnsen & Lenes (2004) found the xylans and galacturonic acids in DIP waters to be good in stabilizing wood resin, even better than galactoglucomannans from TMP.

The reason for the problems with the mixing of TMP and DIP is not clear, but the different pH's of TMP and DIP before mixing might be one reason, as well as the calcium coming from the DIP and causing wood extractives from TMP to agglomerate. With a rise in temperature, wood pitch becomes less tacky and more dispersed, whereas stickies become stickier. However, Castro & Dorris (2004) saw an increased deposition when the pH of a TMP suspension was increased. Dechant *et al.* (2004) suggest that each paper machine would have its optimal operating temperature. Adjusting the pH of pulps to the same level before mixing might also help.

In mechanical pulping, pitch is found as droplets with hemicelluloses, mainly galactoglucomannans, surrounding the droplet as a protective layer (Hannuksela 2004). In deinking, there are mainly fatty and resin acids (Papers I-II), which do not exist as droplets but as free acids or more likely in Na- or Ca-soaps, as their  $pK_a$  varies between 6-9 (McLean *et al.* 2005; Ström 2000). Na-soaps are soluble but Ca-soaps are insoluble and tacky agglomerates.

The earlier studies have not shown what happens when the pulps with different properties, such as pH, are mixed. It seems that there is some kind of agglomeration or adsorption leading to deposition. To find out the interactions between the DIP and TMP components, the mixing of TMP and DIP was briefly studied in Paper II. The dissolved and colloidal material from unbleached TMP was noticed to agglomerate and precipitate in the presence of DIP, or probably adsorb on DIP fiber surfaces. No interactions between wood pitch and stickies were observed when only the filtrates of these pulps were mixed, which supports the adsorption hypothesis. More results are seen in Figs. 9 and 10 below, where unbleached and dithionite bleached TMP and DIP were mixed and centrifuged. The turbidity and pH of the supernatant were measured and wood extractives analyzed by MTBE-extraction followed by gas chromatography.

### Mixing of DIP and unbleached TMP

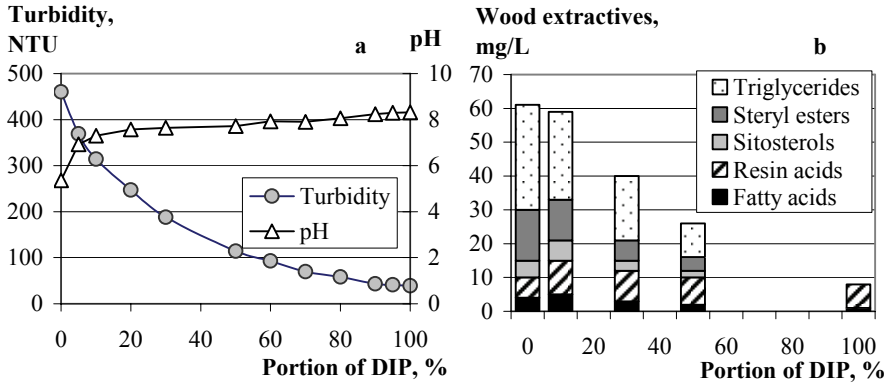


Fig. 9. The effect of mixing DIP with unbleached TMP on (a) turbidity and pH, and (b) wood extractives in the centrifuged supernatant of the pulp mixture (unpublished data).

### Mixing of DIP and dithionite-bleached TMP

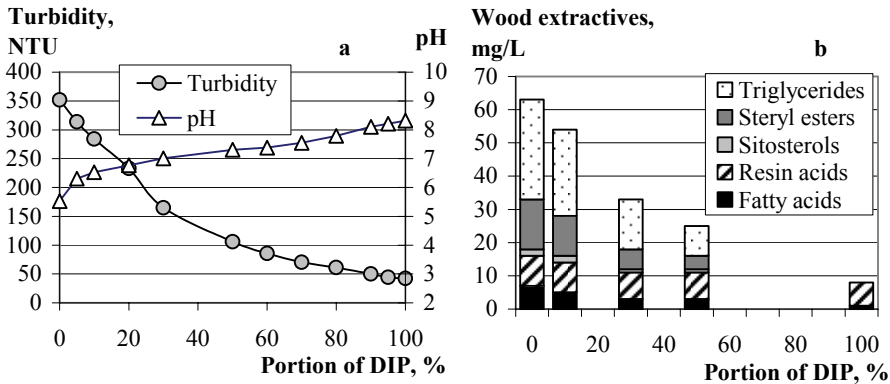


Fig. 10. The effect of mixing DIP with dithionite-bleached TMP on (a) turbidity and pH, and (b) wood extractives in the centrifuged supernatant of the pulp mixture (unpublished data).

Mixing a small amount of DIP in TMP caused a pH shock and a rise in calcium ion level. Zeta potential decreased from -16 mV to -14 mV and the conductivity also rose when DIP was added to unbleached TMP. These changes led to the agglomeration of wood extractives with themselves or onto the fibers. The

presence of fibers seemed essential for precipitation, as precipitation was not noticed when only waters were mixed (Paper II). Adding a small amount of TMP to DIP did not cause a pH shock, because DIP is well buffered by the calcium carbonate. The agglomeration of wood extractives was verified with the analysis of the centrifuged water.

The agglomeration of wood extractives in mixing TMP and DIP might be thought as a precipitation of secondary stickies, which was already discussed in Chapter 3.3.3.

## **4 Control of stickies**

The control of stickies may be roughly divided into two possibilities: Removal of stickies and prevention of the remaining stickies to deposit. Removal of stickies is usually the primary goal, and deposit control is performed to minimize the detrimental effects of the stickies that cannot be removed.

Removal of stickies may happen anywhere where there is a reject stream. Depending on the handling of the reject, stickies are either purged out of the system or recirculated back. The true exit points are usually the pulper rejects, dewatered screening, cleaner, flotation and internal water treatment rejects, and waste water. The removal of stickies almost always means yield losses. The direction in research and development is naturally towards more selective removal of stickies.

Prevention of stickies from depositing may include a number of different actions. The selection of equipment materials may affect significantly the deposition, as well as protecting the materials with chemicals. Different wet end additives may be used to lower the deposit tendency of the stickies. The process is tried to stabilize so that pH, temperature, conductivity or charge shocks do not occur.

### **4.1 Removal of stickies**

Data on the removal of stickies over the whole deinking plant as well as over single process units was collected from eight deinking mills using OMG/ONP mixtures as raw material (Table 3). This kind of data on the removal of stickies of all sizes in different unit operations with an advanced analysis method has been limited to a few studies (Asp 1994; Holmbom 1997; Johansson *et al.* 2003); the other studies have been done with gravimetric extraction or with macro stickies methods.

**Table 3. Data of stickies removal at eight mills; reduction of stickies concentration over the whole deinking plant (Total), and unit operations to the extent they were measured. THF-extraction and HPLC-SEC was used to measure the amount of stickies. In flotation results, the reduction is calculated over one flotation stage (e.g. primary flotation) and in screening and cleaning over the whole system. The total reduction is an average in the cases, where several samples across time were taken (unpublished data).**

Raw material	Concentration of stickies % of dry pulp		Reduction of stickies concentration %				
	Pulper accept	Final DIP	Total	Fine screening	Flotation	Cleaners	Dewatering
60/40	0.47	0.04	91		75...81		
60/40	0.35	0.09	74				
60/40	0.45...0.77	0.08...0.13	83		55...70		
55/45	0.59...0.72	0.02...0.05	95				
50/50	0.33	0.04	88				
50/50	0.66	0.06	91	0	60	65	29
10/90	0.50	0.02...0.07	91	9...55			-6...10
10/90	0.20...0.80	0.02...0.06	92	25	48	-24...49	37...86

The mills in Table 3 had a raw material composition of OMG/ONP varying from 60/40 to 10/90. The raw material composition did not, however, affect the stickies concentration in the pulper accept, which varied between 0.2%-0.8%. The incoming amount of stickies is generally less than the wood pitch concentration in softwoods (Ekman & Holmbom 2000). The fresh water consumption was not among the criteria if the deinking mill removed a lot of stickies or not. The total reductions in stickies concentrations varied from 74-92%. Overall, usually very high removals of stickies were measured. Trying to increase the stickies removal is thus very hard as the present removal is already very high. However, even if the removal rates were very high, almost all of these mills complained about seasonal or constant stickies problems. The portion of deinked pulp in the paper making furnish naturally affects the severity of the deposition.

The removal of stickies in different unit processes varied a lot from mill to mill. Those removals are discussed in more detail in the following chapters, but in general, flotation was consistently effective in stickies removal.

#### **4.1.1 Removal of stickies in screening and cleaning**

Removal of macro stickies is the main purpose of fine screens in deinking plant, although the removal of other big contaminants is also a target. Screening has been reported to remove macro stickies very well (Cao *et al.* 2003; Engert & Haveri 2004, Lee & Kim 2006; Hamann & Strauss 2002; Huo *et al.* 2001; Perrin & Julien-Saint-Amand 2006; Selder 2001). However, Johansson *et al.* (2003) found that even if screens remove 99% of macro stickies, only 10-20% of all stickies are removed. This result is in accordance with the results obtained in Paper VII in a mill balance, where most of the stickies were noticed to be removed in flotations and only a minor part in the fine screening (Fig. 11).

It has been shown that the amount of micro stickies can be increased during screening (Johansson *et al.* 2003; Delagoutte & Brun 2005; Huo *et al.* 2001). That means that part of the macro stickies breaks down into micro stickies due to the shear forces in the pressure screening. Huo *et al.* (2001) showed that screening in several steps produced string-like stickies. Gonera *et al.* (2005) found that PSA's were more susceptible to disintegration than hot melt rubber adhesives, which become spherical in pulping, and are thus more easily separated in screening.

Many parameters affect the screenability of stickies, such as the formulation of the adhesives and mechanical properties, for example the screen basket and foil design (Lucas *et al.* 2004; Lindroos & Puro 2006), and naturally also the operating parameters like reject rate and pressure drop (Griener 2004). It is common that stickies bigger than the slot size extrude through the slots due to the deformability of stickies (Asendrych 2006; Julien-Saint-Amand 2005) Higher pulping temperature produces smaller stickies, which leads to poorer screening efficiency of stickies (Houtman *et al.* 2004). To keep the adhesives large and thus easily screened, the adhesives should have a low deformability meaning a good ability to absorb energy in deformation (Zhao *et al.* 2005).

The design of the screening sequence also affects to great extent how the stickies are removed, e.g. if the stages are organized in cascade or feed-forward mode. Table 3 shows 0-55% reduction in stickies concentration across the fine screening systems.

The density of adhesives is usually near that of water, which makes their removal difficult by cleaners. Huo *et al.* showed (by chloroform extraction) removal of macro stickies up to 75% in a single cleaning step. Perrin & Julien-Saint-Amand (2006) also reported some removal of macro and micro stickies in

high-density cleaning. Bienert (2005) measured 10-20% removal of macro stickies in cleaners.

Asp (1994) studied the removal of different stickies components in screening and cleaning. Styrene butadiene (SB) was not removed in coarse or fine screening, indicating that it is disintegrated into micro stickies in the pulper. EVA, PVAc and acrylates were all removed in coarse and fine screens indicating that they were partially remaining big in the pulper. However, these substances were also removed in flotation indicating that they were also partly ground into micro stickies. SB, EVA and PVAc were also noticed to be removed in forward cleaners at 0.6% consistency to some extent in that study.

The quite limited data of cleaners in Table 3 indicates that reduction in stickies concentration up to 65% was sometimes measured. Sometimes, even an increase in stickies concentration was seen, indicating that particles with lower stickies concentration than the feed ended up in the reject.

#### **4.1.2 Removal of stickies in flotation**

Deinking flotation is designed for ink removal, but it has also been noticed to be good for stickies removal. Deinking flotation is especially good for micro stickies removal due to the optimal size range for flotation, and removals up to 96% have been measured with varying methods (Delagoutte & Brun 2005; Johansson *et al.* 2003; Lee & Kim 2006; Selder 2001). Macro stickies removals of 10-70% have been reported in post and secondary flotations (Bienert 2005; Engert & Haveri 2004, Geistbeck & Wiese 1997; Glover *et al.* 2001; Huo *et al.* 2001; Cao *et al.* 2003). Holmbom (1997) reported good removal of SB-latex and PVAc in pre-flotation, and MacNeil *et al.* (2004) showed very good fatty acid removal in flotation, but quite poor resin acid removal. Table 3 showed that the reduction in stickies concentration at the eight mills studied varied from 48-81%. Despite the great variations from mill to mill, flotation gave the most consistent results in good stickies removal compared to the other unit processes shown in Table 3.

Based on the optimal size range for flotation, it would seem rational that micro stickies were removed better than macro stickies in flotation. That has not been, however, proven before. In Paper VI, 32% of stickies retaining on 76  $\mu\text{m}$  wire were removed in laboratory flotation and 87% of stickies passing the 76  $\mu\text{m}$  wire were removed. This verifies the hypothesis that flotation is more suitable for micro stickies removal. The fraction containing stickies smaller than 76  $\mu\text{m}$  was



further divided into smaller fractions, and in all those fractions the removal of stickies in the flotation was 82-90%.

Johansson *et al.* (2003) detected a major reduction of stickies in the pre-flotation with additional, although lower, removal in post-flotation and thickening. Overall removal of stickies in flotation was 78% in that study. Pawlowska (1999) measured 62-85% removal of chloroform/MEK-extract in laboratory deinking flotation of mixed office papers depending on the flotation aid. Perrin & Julien-Saint-Amand (2006) reported some removal of macro stickies in post-flotation and up to 60% removal of DCM-extract in a single flotation step.

An overall picture of the stickies removal in different stages was obtained in Paper VII. The flow of stickies in a two-loop flotation system was determined for one mill, and a Sankey-diagram was drawn (Fig. 11).

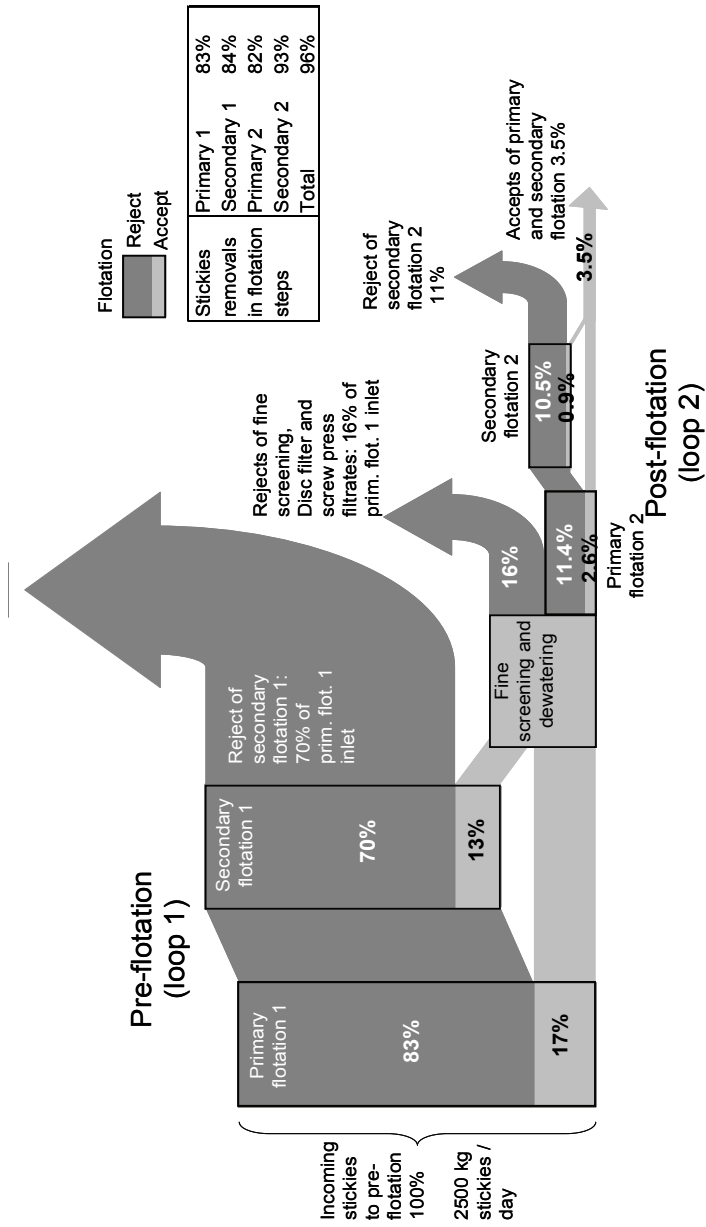
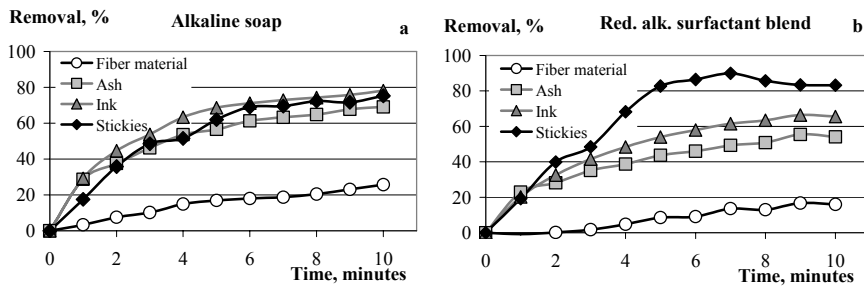


Fig. 11. Stickies mass balance over a flotation system (Paper VII).

In Figure 11, the stickies are presented as the mass flow of stickies. The amount of stickies calculated as percentage of the incoming stickies into pre-flotation 1 are also shown in each flotation step. The stickies removal in the flotation units varied from 82-93%. That is in the same range as what has been analyzed in other studies (Johansson *et al.* 2003; Pawlowska 1999; Perrin & Julien-Saint-Amand 2006). The diagram shows clearly that the majority of stickies entering the pre-flotation are removed in the flotations, and only 16% of stickies entering the pre-flotation are removed in fine screening and dewatering. That supports the hypothesis that majority of stickies are micro stickies.

The overall stickies removal in flotations, fine screening and dewatering was 96.5%. However, due to recirculation of disc filter and screw press filtrates back to a stage before the pre-flotation, this value includes the repeated removal of the recirculated stickies, and thus the overall removal rate would be lower if calculated using the original stickies content in the pulp. The main exit point of stickies is the reject of secondary flotation 1. However, the primary flotation 2 has the greatest effect on the final amount of stickies.

The flotation is designed for ink removal, but according to these results, it also removes stickies very well. Ash is also removed in flotation to some extent, but fibers, being hydrophobic, are not removed very much, although even that small removal should be avoided. What is then the position of stickies removal compared to the removal of other substances? That was studied in Papers VI-VII, where the kinetics of stickies, ink, ash and fiber removal in flotation were studied with two different deinking chemistries by taking samples from a laboratory flotation every minute (Fig. 12).



**Fig. 12. Removal of fibres, ash, ink and stickies in laboratory flotation as a function of time for two pilot pulps pulped with different chemistries: (a) alkaline soap chemistry and (b) reduced alkaline surfactant blend chemistry (Paper VII).**

Stickies were removed in flotation faster or at the same rate as ink (Fig. 12), most likely due to the same mechanism, by which ink was removed. That was discussed in more detail in Chapter 3.3.4. The removal was faster in the beginning of the flotation, and as time progressed, the removal rate slowed. That is most likely due to the decreasing stickies concentration making the probability of collision between ink and air bubbles and attachment smaller. The backflow of particles from the froth back to the pulp suspension (Beneventi *et al.* 2006) could also be the reason for the plateau in the removal curve. However, the stickies removal against total solid loss was almost linear, which means that the selectivity remained the same throughout the flotation, and the removal of all substances slows down after certain point.

The ash removal was higher in Fig. 12 than in the laboratory flotation of real mill pulp (Paper VII) or the laboratory flotation of screw press filtrate (Paper VI); in those experiments a different laboratory device was used, too. However, it can be said that the stickies have a higher affinity for removal in flotation than ash. That is most likely due to the more hydrophobic character of stickies and the fact that fillers might be too small to be removed in flotation unless they are not agglomerated with other substances.

The removal of fibers stayed linear with respect to time, which indicates that the fibers, being hydrophilic are mainly removed to the froth with the water. The ink removal and stickies removal correlated well, which was already discussed in Chapter 3.3.4.

The addition of cationic fixative or polymer just before flotation can help the removal of stickies to some extent (Paper VI). The fixatives or polymers most likely make the stickies agglomerate either with themselves or with other papermaking components, and thus better removable by flotation. Similar observations have also been made elsewhere: Lyche *et al.* (1998) found poly-DADMAC fed prior to flotation to be good in helping the stickies removal in flotation. Zhao *et al.* (2003) also noticed that poly-DADMAC together with additional fillers increase the stickies removal. Spedding (2002) added hydrophobic mineral in disperger, which was claimed to form micro agglomerations with stickies, which would be removed in flotation. Lee *et al.* (2005) observed that the presence of fibers is crucial for cationic polyacrylamide to help stickies to attach air bubbles.

### **4.1.3 The effect of pulper chemistry**

Deinking chemistry is important for stickies removal in a deinking mill. The stickies are detached from their substrate in the pulper for the first time, and thus the conditions in the pulper are very important for the performance of the subsequent unit processes. In this thesis, the stickies removal in flotation with conventional alkaline soap chemistry and reduced alkaline chemistry was researched.

One of the most important driving forces towards neutral deinking is the potential for cost savings in pulper chemicals. Often sodium hydroxide, peroxide, chelants, and some or all of the sodium silicate are no longer added to the pulper. The surfactant chemistry then becomes essential to maintain deinking performance under neutral conditions. In true neutral conditions, only surfactant is added while in reduced alkaline deinking also sodium silicate is added. Chezick *et al.* (2004) reported savings of \$5-\$10 per ton of DIP. Schmid (1995) calculated 40-50% cost savings in chemicals when a mill changed its chemistry from alkaline to neutral.

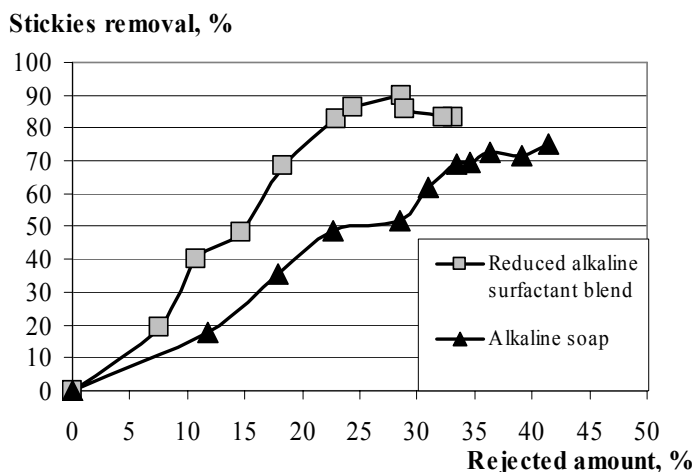
Neutral or reduced alkaline deinking has been attempted many times in the past with varying success in laboratory, pilot and industrial trials of reduced alkali, neutral and true neutral deinking with synthetic surfactants or silicone derivatives (Schmid 1995, Schwinger 1995; Pegelow & Nellessen 1998; Süß *et al.* 1995; Lapierre *et al.* 2002, 2004a, Nellessen 2006; Rosencrance *et al.* 2005). One benefit of neutral deinking is the better removal of flexographic inks under neutral conditions (Galland *et al.* 1997; Ryu & Lee 2003). It seems that the solution is the reduced alkaline surfactant chemistry with silicate (Rosencrance *et al.* 2005; Lapierre *et al.* 2006), because the silicate seems to be important in disintegration of the recovered paper by lowering the friction between the fibers and promoting the ink flotation selectivity by the better adhesion of ink particles to the surface of air bubbles and the increase in the fillers, fibers and fines drainage rate through the froth (Beneventi *et al.* 2006).

The effect of repulping at a lower pH with surfactants was noticed to have three main effects on stickies. The first was that stickies do not break up into as small particles as with alkaline soap chemistry. This was found on both pilot and mill-scale (Paper V). Very limited measured data has earlier been reported: Fewer macro stickies or deposition from the pulp, and colloidal and organic load in waters has been shown to result from deinking in lower pH (Dingman 2000; Ryu & Lee 2003; Haynes *et al.* 2004; Lapierre *et al.* 2004b). The lower amount of

macro stickies could be due to the better removal in screening due to the stickies being larger (Ackermann *et al.* 1999).

The second effect of reduced alkaline surfactant chemistry was the lower deposit formation tendency of the pulp (Paper V). The result was obtained with a laboratory tester imitating the drying section of paper machine, as the mill trial was too short to observe the effects on runnability. The surfactants possibly form a hydrophilic layer around the stickies making them less likely to deposit. The hydrophobic end of the surfactant molecule is attached to the hydrophobic stickies particles while the hydrophilic end is oriented outwards making the particle a more hydrophilic surface. This layer seems to tolerate the drying of the paper on a hot plate. Luo & Horacek (2001) also found surfactant blend chemistry to produce lower amount of deposits on both laboratory and full scale.

The third effect was the better removal of stickies in flotation, which was proven on laboratory (Fig. 13) and pilot scale (Paper VII).



**Fig. 13. Stickies removal, as %, against the rejected amount of solids, as %, with alkaline soap chemistry and reduced alkaline surfactant blend chemistry (Paper VII).**

Figure 13 shows that stickies were more selectively removed when the reduced alkaline chemistry was used in the pulper, which is in accordance with the findings of Lyche *et al.* (1998) which showed surfactants being better in stickies removal in flotation than soap. This could be due to the surfactants better detaching the stickies from the substrate in the pulper, or due to the stickies having different surface chemistry properties, that make them easier to attach to

the air bubbles in the flotation. The alkaline soap chemistry seems to be less selective, and collecting all solids, whereas the reduced alkaline surfactant blend chemistry has a higher affinity for stickies. In alkaline soap chemistry,  $\text{Ca}^{2+}$  ions play a significant role in collecting the ink and making them able to attach to the air bubbles. When surfactants are used,  $\text{Ca}^{2+}$  ions are not that important (Beneventi & Carré 2000).

It is important to add the surfactants already to the pulper. If the surfactants are added just before flotation, they make the surfaces of the stickies more hydrophilic, which is not desired if they are to be removed in flotation (Ling 1994). If the surfactants are added to the pulper with a high consistency, this kind of effect is not seen (Fig. 13). Also, the modification of surfactants into such that they do not affect the surface properties of stickies, may lead into good results (Li *et al.* 1996).

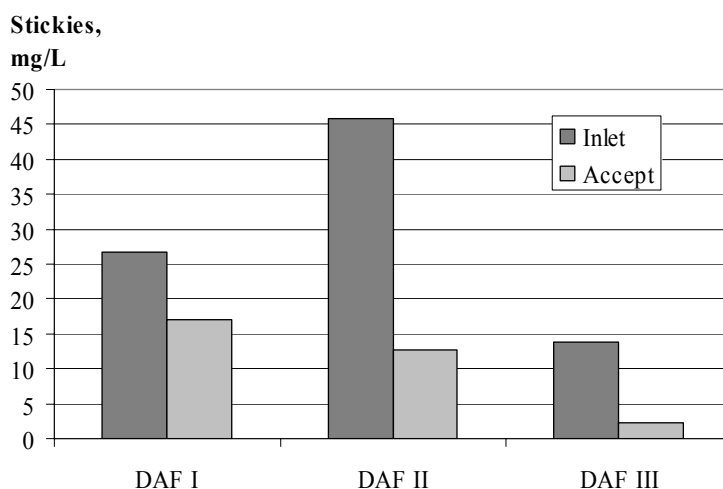
#### **4.1.4 Internal water treatment**

The purpose of internal water treatment is to prevent accumulation of contaminants in the water loops and thus lower the contaminant load going to the paper machine. Internal water treatment is most commonly done by dissolved air flotation (DAF), which treats a part of the water in the water loop. There can be up to four DAF units (1<sup>st</sup> loop, 2<sup>nd</sup> loop, paper machine loop, effluent, sludge) in a deinking mill depending on the quality of the pulp produced. DAF is not selective like deinking flotation. Ben *et al.* (2004) reported yield losses of 6-8% due to internal water treatment. The non-selectivity is derived from the micro bubbles produced when the dissolved air is released to the water followed by a pressure drop which creates very small bubbles. These micro bubbles usually collect everything possible and carry it to the froth, like a comb leaving just the water behind.

The waters in the water loops are the filtrates of disc filters, screw presses or other thickeners or washers. Dewatering and washing have been reported to remove micro stickies (Delagoutte & Brun 2005). Especially PVAc and EVA were detected to end up in the filtrate (Asp 1994). Also Selder (2001) detected micro stickies in the filtrate from dewatering. Kappen (2005) measured the highest amount of potential stickies, measured by INGEDE Method 6, in the first loop of deinking plant, with lower amounts in second and the lowest in the paper machine loop. The measured amount of potential stickies was very high, 100-500 mg/L. Garver *et al.* (1997) has measured 70-120 mg/L of ether extractives (wood

extractives) in paper machine white waters. Stickies ending up in the filtrates is logical, as a major part of the stickies were detected to be very small (Papers IV-VI). The stickies are not, however, dissolved in water to any great extent, so their removal from the filtrates should be possible with the existing technology.

The detected amounts of stickies in DIP filtrates by Kappen (2005) and Garver *et al.* (1997) seem very high, based on the fact that stickies were not found to exist as dissolved or colloidal, but as small agglomerates. The stickies amounts across three DAF's were detected by freeze-drying the waters until they were dry (one-two weeks) and extracting the dry residues with THF, followed by HPLC-SEC. Fig. 14 shows the stickies removal at three different DAF's at two deinking mills.



**Fig. 14. Stickies concentrations, mg/L in three DAF's from two different mills, measured by THF-extraction and HPLC-SEC (unpublished data).**

15-45 mg/L of stickies were found in the DAF inlets (Fig. 14), which is notably less than what was reported by Kappen (2005) and Garver *et al.* (1997). The differences are derived from the different analysis methods used. Pawlowska *et al.* (1999) measured gravimetrically 4-17 ppm extract (chloroform/MEK) in clarified process water, which is in the same range what was analyzed here.

Reductions of the stickies concentrations in DAF's I, II and III were 36, 72 and 83%, respectively. DAF's I and III used cationic polyacrylamide for flocculating the particles before the unit, while DAF II did not use any chemicals.



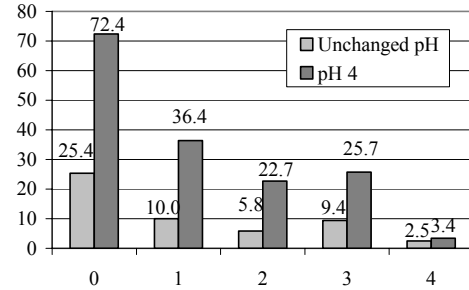
DAF I was from a different deinking mill than DAF's II and III. No clear explanation for the poor removal was found.

DAF is thus also effective for stickies removal. The stickies removal was to some extent dependent on the suspended solids removal, which gives evidence that DAF is not at all selective, and is not based on the attachment of particles on bubbles based on hydrophobicity. Ben *et al.* (2003) also found that DAF is very good in removing stickies and wood extractives. The removal of the extract in the DAF was 9-77%. Ben *et al.* (2004) found DAF's to remove small-sized stickies (passing 400 mesh = 38  $\mu\text{m}$  screen). Perrin & Julien-Saint-Amand (2006) measured up to 60% removal of micro stickies (DCM-extract of fines) in DAF. They also measured sludge thickening to retain about 95% of the DCM-extract, meaning that stickies removed in the DAF are not recirculated back even if the filtrate from sludge dewatering is recycled. Macro stickies removals of 50-100% have been reported in DAF's (Bienert 2005; de Jong *et al.* 2006; Engert & Haveri 2004).

The chemicals used in DAF greatly affect the performance of a DAF. Bentonite/PAM (polyacrylamide) chemistry is widely used in DAF's at deinking mills. Aluminum-based chemicals are another group of chemicals quite commonly used in DAF's (Capdepon *et al.* 2002) The  $\text{Al}^{3+}$  ion catches dissolved and colloidal substances better than e.g. bentonite (Paper I). Huo (2002) noticed model micro stickies to have an electrical double layer, which may be destabilized with electrolytes, such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  or  $\text{Al}^{3+}$ . If also real stickies were in such a form, that would explain the good performance of aluminum chemicals.

The ability of different chemicals to coagulate and flocculate dissolved and colloidal substances was tested on laboratory scale with the turbidity difference method (Fig. 3), which measures colloidal substances sensitive for pH shocks (mainly wood extractives, Fig. 4a). The results are seen in Fig. 15 below.

**Residual turbidity,  
NTU**



Sample number	Chemical	Dose, ppm
0	none	-
1	Bentonite/A-PAM	30/2
2	Cat. fix / C-PAM	20/2
3	Poly-DADMAC	30
4	PAC	400

**Fig. 15. Effect of different coagulation and flocculation chemicals on the turbidity difference of paper machine loop DAF inlet (Paper II). A-PAM = anionic polyacrylamide, C-PAM = cationic polyacrylamide, PAC = polyaluminum chloride.**

Fig. 15 clearly shows that polyaluminum chloride coagulated the colloidal substances and wood extractives best. All chemicals enhanced the flocculation compared to the blank sample without any chemicals.

Richardson & Grubb (2004) reported 80-90% removal of fiber bound and colloidal wood extractives in a DAF, while soluble extractives were removed by only 30%. There also, PAC showed its ability to remove water soluble extractives. Basta *et al.* (2004) found low dosages of organic cationic polymers to be good in DAF for treating DIP filtrates. In a study by Pelzer & Künzel (2006), over 99% of PAM used in internal water treatment was detected in the reject of the dissolved air flotation.

Saarimaa *et al.* (2006) reported that up to 90% of pitch could be removed by DAF at pH 5, when most of the extractives are in colloidal form. They also found PAC to be a very effective coagulant lowering also the charge in addition to extractive removal. Sain *et al.* (2002) also found aluminum-based chemicals, chitosan and zeolite combined with PAM to be effective in removing turbidity in deinking mill waters.

The effect of internal water treatment on the total mill balance is not very well known. Steady-state simulations showed that 60% removal of extractives in an internal water treatment unit purifying paper machine press section filtrate led to a 66% reduction of extractives in the final deinked pulp water phase (Paper II). Stickies were not included in the model so the effect of stickies removal could not be simulated.

## **4.2 Prevention of the deposition of the stickies**

Preventing the remaining stickies in the final DIP from depositing is usually very difficult, because the reason for the deposition is not always clear. The theories of adhesion involve the mechanical trapping due to the surface roughness, adsorption theories with van der Waals forces and London dispersion forces, chemical theories with acid-base interactions and hydrogen bonding, diffusion theories, electrostatic theories with the electrical double layer between the substrate and adhesive, and rheological theories with pressure sensitive adhesives (Allen 2005). Unfortunately, there is not enough information on which of these theories applies to the adhesion between stickies and the paper machine equipment. The actions that prevent deposition are thus more or less found by trial and error. Furthermore, sometimes the problems disappear with the reason remaining unclear.

Stabilizing the process and avoiding sudden changes is many times the key to success. Temperature and pH of e.g. dilution or shower waters should be the same as where the water is added. Changes in various chemical parameters, such as conductivity, charge or zeta potential might also be dangerous. In drying section and calenders, the temperature plays a very important role in where the deposits form.

The deposition tendency of the adhesives is also dependent on the substrate. For example, Fike & Banerjee (2004) found that the adhesion between an adhesive film and carbon steel was much weaker than the adhesion between the adhesive film and stainless steel. Material selection is thus very important in preventing deposition. A variety of different surface materials exists to make the surfaces more difficult for stickies to deposit.

Different chemical additives are many times used to prevent the deposition. The additives include organic and inorganic substances, and they are applied on the wet end of the paper machine to make the wires or rolls more hydrophilic to protect them from deposition. The fixing and retention aids may also be selected so that fewer problems occur. The following chapters discuss these additives in more detail.

### **4.2.1 Fixing and retention**

Selection of the appropriate wet end chemicals may reduce the stickies deposition, if the stickies are small enough and trapped inside the paper sheet, or if the

chemicals form a protective layer around the stickies preventing deposition. The higher retention of stickies also prevents the accumulation of stickies in the white water, and makes the stickies exit the system with the paper. Thinking globally, this will introduce the stickies again to a papermaking system if the produced paper is again recycled.

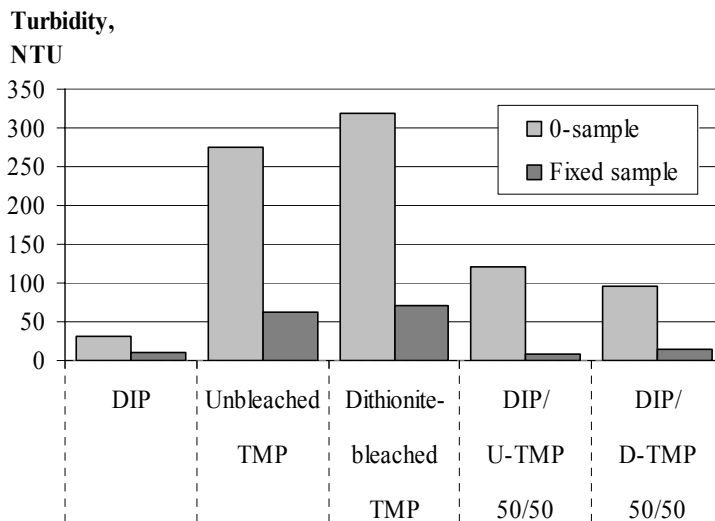
Fixing of detrimental substances with high-charge, low molecular weight organic polymers on the fiber may be thought as the first step of retention. Too large particles do not stay on the fiber and end up depositing, but by microfixation of the stickies as small as possible with optimized polymers, machine downtime due to wire cleaning can be reduced (Philippaerts 2000; Hättich *et al.* 2002). Ward *et al.* (1994) also came to the same conclusion: In order to reduce the stickies problem, the stickies have to be made small with a non-ionic dispersant and fixed to fiber as small particles with a high charge density fixative. Hamann *et al.* (2004) found that the fixing of coated broke reduced the quantity of materials deposited. Gruber *et al.* (2000) found aluminum sulphate and cationic fixatives to reduce wet deposition of stickies. Poly-DADMAC together with acrylic acid or acrylamide is patented for deposit control (Song *et al.* 2006). Huo (2002) noticed poly-DADMAC to adsorb on the surface of model micro stickies and prevent the agglomeration of the stickies. In the presence of fibers, poly-DADMAC was shown to form fiber-stickies-flocs.

The use of fixatives does not always have positive effects: Castro & Dorris (2004) found polyethylene imine (PEI) to increase the deposition of stickies. Cationic coagulants are, furthermore, used in secondary stickies deposition methods (Carré *et al.* 1998; INGEDE Method 6).

Bentonite is also many times used as a retention aid, and it has been reported to be able to reduce stickies problems (Putz *et al.* 2003; Sjöström *et al.* 2004).

Cationic polyacrylamide (C-PAM) is very commonly used as a flocculant in retention programs. C-PAM has been shown to be able to fix model secondary stickies (never-dried polymethacrylate dispersed in water) on the fibers and reduce thus deposition (Li & Zhan 2005). They also found that cationic starch destabilizes model secondary stickies, but also adsorbs on the sticky surfaces and reduces tackiness, while calcium may boost the deposit formation. Huo *et al.* (2001) also found that retention aids (polyamine flocculant and C-PAM) reduced the deposition on a polyester paper machine wire in a laboratory test. LeRoux *et al.* (1997) have also shown the importance of appropriate retention aids in stickies control.

The fixatives may make the interactions between mechanical pulp and DIP stronger. Fixing was better when mechanical pulp was mixed with DIP. Fixing the pulps separately with a PAM-based short chain fixative at a dosage of 3 kg/t resulted in higher turbidity after centrifugation and thus a poorer fixing result compared to a situation where the mixture of pulps was fixed (Fig. 16). That may be explained by the coagulation of wood extractives when the pulps are mixed (see Figs. 9 and 10), which results in better performance of the fixative. The wood extractives precipitate either with each other or onto the surfaces of fibers.



**Fig. 16.** The synergistic effect of fixative, when DIP and either unbleached or dithionite-bleached TMP are mixed, on turbidity. Turbidities are measured from the water phase after centrifugation (unpublished data). U-TMP = unbleached TMP, D-TMP = dithionite-bleached TMP.

#### 4.2.2 Fillers and talc

Inorganic particles are often mentioned in literature as adsorbing on the surface of the stickies and thus making the stickies more rigid and thus not so tacky anymore. Talc is maybe the most known inorganic particle used to reduce the problems due to stickies (Biza 2001; Yordan *et al.* 2004). Talc is a hydrated magnesium silicate and has plate-like crystalline structure. It is added to the second loop press or disperger in the deinking plant or in the wet end of a paper machine. As a very

hydrophobic mineral, talc is adsorbed on the surface of stickies making them non-sticky. Talc has higher affinity to adsorb micro stickies than GCC (ground calcium carbonate) or bentonite (Yordan *et al.* 2001). However, talc works mainly with micro stickies, and not with macro stickies (Yordan & Maat 1997). Terpene may be used with talc to increase the affinity of the contaminants for the talc (Mah 2005). Willför *et al.* (2000) and Guéra *et al.* (2005) have shown that talc can also adsorb wood extractives. Le *et al.* (2002) also found talc to be able to adsorb hydrophobic substances. Reynolds & Yordan (2002) reported good experiences of talc in reducing stickies problems in two mill cases.

Other minerals have also been noticed to have detackifying characters. Klungness *et al.* (2004) found that precipitated calcium carbonate (PCC) passified stickies either by fiber-loading or direct loading. The drawback of calcium carbonate is that it decomposes at a pH below 6.5, while talc is not pH sensitive at all. Selin (2005) found that kaolin, GCC and PCC can adsorb unstable pitch from peroxide bleached TMP. Sitholé *et al.* (1997) noted that kaolin (clay) inhibited deposition of stickies in a laboratory test done at 10% consistency. Vogel (2002) found diatomite to be good in stickies pacification. Gruber *et al.* (2001) found that talc may also increase the deposition of stickies, and calcium carbonate decrease.

Aluminum chemicals, bentonite and talc added in the wet end of a paper machine reduce the amount of COD in white water (Sjöström *et al.* 2004). Putz *et al.* (2003) found talc and bentonite to be able to reduce the deposition of stickies in wet conditions. By coagulating the filtrate with polyvinylamine, the deposition tendency was reduced by up to 90%. Beaudoin *et al.* (1998) also noticed that bentonite prevents stickies problems on a paper machine.

#### **4.2.3 Other passivators**

Some chemicals may disperse the smallest stickies into stable particles that are no longer likely to deposit. A stabilizing layer around the stickies particles may be formed that protects the particles from deposition.

Literature gives some examples of this kind of detackifiers or dispersants. Water-soluble polymers consisting mainly of acrylamide and also vinyl acetate is patented (Kurowsky *et al.* 2002). Nguyen *et al.* (2002) used a styrene/methacrylic acid copolymer with calcium ions to inhibit deposition. An EO/PO (ethylene oxide / propylene oxide) block copolymer is also patented: It is claimed to stabilize the dispersion of the hydrophobic particles and thus prevent deposits (Agarwal *et al.* 2001). Miller *et al.* (2004) reported good mill results in reducing

the stickies problem by adding a medium molecular weight, non-ionic solution polymer that adsorbs on the surface of the hydrophobic particles. That combined with a wire passivator led to good results. Nguyen & Dreisbach (1996) also demonstrated that treating forming wires with a polymer that makes the wire material less hydrophobic can reduce the deposits on the wires. Polyvinyl alcohol is known to reduce deposition on the wet end of the paper machine.

Corcoran (2000) studied electricity in preventing deposition of stickies in his doctoral thesis. Electrohydraulic discharge under water was reported to decrease the tack and hydrophobicity of stickies at two mills. The mechanism involves oxidation of the polymer surface.

Welkener *et al.* (1993) claimed that water soluble wood extractives could reduce the deposition of colloidal pitch or stickies by adsorbing on the surface of the colloids and stabilizing them by sterically or by charge neutralization. Starch, both neutral and cationic, was also noticed to adsorb on the surface of model micro stickies preventing deposition (Huo 2002).

Enzyme technologies in stickies treatment are based on the reaction where the enzyme, e.g. esterase, hydrolyzes the ester bond that makes some of the adhesives sticky (Wang *et al.* 2006). Seifert & Zimmermann (2004) estimated that 70-90% of stickies are based on ester compounds. Polyvinyl acetate, for example, is hydrolyzed into non-sticky polyvinyl alcohol and acetic acid. The enzymes are added either in the stock or on paper machine clothing (Jones 2005). Severtson *et al.* (2002) found that the use of wet strength resin in paper on which the adhesive is used could prevent the disintegration of the adhesive during pulping. This would help the stickies removal in screening. The use of AKD (alkyl ketene dimer) sizing agent has also been reported to have similar effects.

Dicyandiamide and some non-ionic polymers as well as some cationic fixatives showed good potential in reducing deposition with the drying section deposition tester (unpublished data). This result, however, was not verified in mill trials. The laboratory tests support the idea of a protective layer forming around stickies that inhibits the deposition even at the high temperatures that occur in the drying section of paper machine.

Natural stabilizers for wood pitch in mechanical pulping are galactomannans and galactoglucomannans, which form a protective layer around a pitch droplet making it sterically stable (Hannuksela 2004). The natural substances may also cause problems: Sjöström *et al.* (1987) found that the low molecular mass components may absorb on the surface of the adhesives making them more soft and sticky.

No universal stickies passivator seems to exist, but the chemicals mentioned in the literature might help in certain cases. The problem is usually so mill-specific that the treatment programs are thus also mill-specific. Mechanical things might also help, such as lowering the calender temperature as was reported by Allen & Ouellet (2006). The stability of the process with respect to pH, temperature and charge conditions is extremely important in reducing stickies problems.



## 5 Concluding remarks

A variety of different methods to measure stickies exists. Some of them, e.g. macro stickies measurement methods, are standardized. All of the methods measure slightly different things. The first aim of the thesis was to develop an analysis method that would measure the total amount of stickies. The second aim was to determine the size distribution and nature of stickies, as it is important in order to properly focus the control strategies on the right pulp fraction. The third aim was to determine the removal of stickies in different process units and to find ways to increase their removal.

Solvent extraction followed by HPLC-SEC and ELS detector was found to be a viable method for measuring the amount of hydrophobic polymeric material, i.e. stickies in deinked pulp or deposits from paper machines. Pyrolysis-gas chromatography-mass spectrometry with the amount of individual stickies compounds gives about the same results as the HPLC-SEC ELS-system, which gives the sum of the polymers. In flotation, ink measurements may also be used for estimation of the amount of stickies. Absolute values cannot be determined through only ink measurement, but trends in stickies removal in flotation can be estimated.

The majority of stickies are micro stickies passing the 38  $\mu\text{m}$  wire. Macro stickies are also present, but their content is generally lower than the content of micro stickies. Only trace amounts of stickies were found in centrifuged water, which contains only dissolved and colloidal substances, such as wood extractives. The size of stickies depends not only on the sampling point, but also on the deinking chemistry: Alkaline soap releases more micro stickies than reduced alkaline surfactant blend chemistry.

It was earlier believed that dissolved and colloidal stickies, i.e. potential secondary stickies, agglomerate and cause deposits due to changes in pH, temperature, charge, etc. Based on the new information about the size of the stickies, this cannot be true. The potential secondary stickies may actually be fatty and resin acids, which are known to agglomerate at such process changes. In mixing of mechanical pulp and deinked pulp, agglomeration of wood extractives was noticed. The other possibility is that the changes in pH, temperature, charge etc. cause the micro stickies to agglomerate and cause problems. Whichever possibility is true, the stability of the process with regards to pH, temperature, charge and chemical conditions is in any case important for deposit prevention.

Ink and stickies might be attached to each other in some cases, as they are both hydrophobic and can thus agglomerate. Furthermore, ink binders are one source of stickies, and it is logical that they stay attached to the black ink particles throughout the deinking process. Stickies and ash may also be attached to each other to some extent, because in many cases they behave similarly. The main part of ash is, nevertheless, stickies-free.

Flotation is very effective in removing stickies, especially micro stickies. Ink is also very well removed in flotation with a similar or slightly lower efficiency than stickies. The good floatability of micro stickies and ink is due to the same mechanism for removal: They are both hydrophobic and have optimal size distribution for flotation – from a few micrometers up to about 100  $\mu\text{m}$ .

Pulper chemistry is the primary way of affecting the stickies removal in flotation, whereas additives fed just before flotation may be used to enhance the stickies removal to a smaller extent. Reduced alkaline surfactant blend chemistry was more selective in stickies removal than conventional alkaline soap chemistry. The non-ionic synthetic surfactants also have slightly detackifying effect on stickies.

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## Original papers

- I Sarja T, Zabihian M, Kourunen P & Niinimäki J (2004) New method for measuring potential secondary stickies in deinked pulp filtrates. *Water Science and Technology* 50(3): 207-215.
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- VII Sarja T, MacNeil D, Huber P & Niinimäki J (2007) Removal of stickies in flotation. Progress in paper recycling, accepted 2007.

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