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Determination of Distribution of Fines in a Paper Structure using Fluorescence Microscopy - an introduction

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Abstract

When making paper, fibers and additives are suspended in water to a fiber suspension. The sheet is formed by draining a specific amount of suspension through a wire-cloth. The procedure is well known, but the underlying mechanisms are not fully understood. To understand how the different particles such as fines, fibers, retention aids and other additives interact with each other, further research is needed. This knowledge is important because in the production of paper, the retention and the distribution of fines and additives within a paper structure are vital parameters for the properties and also for the profitability of the final product. In this study fluorescence microscopy was used to study fines from bleached kraft pulp which were labeled with fluorophores. When the fines exhibit fluorescence we can study their individual trajectories and understand more about the interactions between fibers, fines and additives in different chemical environments. Fines from bleached kraft pulp have no fluorescent properties and therefore it is necessary to bind a fluorophore to the material. It was difficult to find a suitable fluorophore which binds covalently to the cellulose, the dominating part of fines. The result from this study was that the labeled fines did exhibited fluorescence. As the fines were aggregated no individual trajectories could be analyzed with fluorescence microscopy. Further development of the technique for labeling fines must be carried out to avoid aggregation of fines.

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1. Background

When making paper, fibers and additives are suspended in water to a fiber suspension. The sheet is formed by draining a specific amount of suspension through a wire-cloth. The procedure is well known but to understand the mechanisms involved we need to understand how the different particles such as fines, fibers, retention aids and other additives interact with each other. Being able to track them would increase the understanding of the mechanisms involved. To label a specific substance with fluorophores and then study it using a fluorescence microscope would be an excellent way to follow the substance during the process. Fines contribute to many properties of paper. To further study their role in the papermaking process fluorescence microscopy may be used. The first step is to develop a good method to label the fines and study their trajectories. It is possible to add labeled fines to the slurry and study how they interact with fibers and additives. To mark substances with different fluorophores that emit light at different wavelengths would provide a deeper understanding of the interactions that occur between the various substances in the slurry. It's a long process before it is possible to make such an extensive study, but to start with the labeling of fines open the possibility of a deeper understanding of papermaking.
2. Introduction

2.1 Paper

Papermaking was brought to Europe by the Arabs around the year 1000 with its origin in China one thousand years earlier. Worn cotton and linen fabrics were torn apart and suspended in water to a fiber suspension. In China they used textile remains and fibers from plants. By draining the suspension through a thin cloth a sheet was formed. The procedure was time-consuming. At the time of the French Revolution, communication grew rapidly and newspapers became more important. The Frenchman Nicolas Louis Robert constructed the first machine that made paper and it was a success because it produced “well felted” paper. In the $19^{\text{th}}$ century cocking equipments came that could make paper fibers from wood chips. These were developed to the factories that produce paper in the $21^{\text{th}}$ century. The main source for paper today is fibers from hardwood and soft wood. Recycled paper is also an important source in the industry. [1]

Cellulose, hemicelluloses and lignin are the building blocks for wood fiber. The building blocks differ in several ways. Cellulose is a linear polysaccharide while hemicellulose has small side branches. Components of cellulose is only the monomer glucose while hemicellulose are built from several different monomers where the composition varies from different sorts of wood. Cellulose is the component that gives the wood its strength because of its stiffness and hemicellulose gives the wood flexibility because of its branched structure. Cellulose builds crystalline micro fibrils which in turn are arranged in fibrils and then in fibers, the construction is shown in figure 1. [2, 3, 4]

![Figure 1: Construction of a wood fiber, from the fiber all the way to the molecule. The components are as follows: A - fibers, B - crosssection fiber, C - fibril, D - micro fibril, E - crystal, F - unit cell, G - a cell unit bios (two glucose monomers). [4]](image-url)
The building block that binds the fibers together is lignin. Lignin is an aromatic hydrocarbon that has a complex three-dimensional structure. Aromatic hydrocarbons can adsorb and emit light and are therefore a source of auto fluorescence. This is why only bleached kraft pulp fines are of interest in this study because it contains a limited amount of lignin and will not interfere with the fluorescence microscopy analysis. [5]

The underlying mechanisms for papermaking are development of hydrogen bonds which forms when the paper dries. The hydrogen bonds give the paper strength as it dries. The rewetting can be prevented by adding chemicals that covalently bind to the fibers or making the surface hydrophobic. When a pulp fiber dries, fines will attach to fibers and also form aggregates. When they then are rewetted, they will not swell as much as a never dried fiber, well known phenomena called hornification. A consequence of hornification is that the fines that are attach to the fibers, will remain stuck to the fiber surface even after rewetting. The fines that are aggregated will also remain in this state. [6, 7]

2.2 Surface and Colloid Chemistry
The chemistry behind papermaking depends on surface and colloid chemistry. Surface tension, capillary forces, colloid stability is some of the mechanisms that are behind the chemistry in papermaking.

2.2.1 Surface Tension and Capillary Forces
Molecules at an interface have higher energy than those inside the material. To lower their energy they try to minimize their surface. This is what happens when a liquid adopts a spherical shape when poured on a solid phase for example or when water bulges out over the edge of a beaker. This is called surface tension. When looking at paper there are thousands of capillaries, from tiny pores in the fiber walls to the larger pores between the fibers. These pores get filled with water due to capillary forces that are a consequence of surface tension. This is because surface tension leads to a pressure in the fluid that is different from the ambient pressure. The water is drawn into the pores until the pressure is equal on both sides. [4, 8]

2.2.2 Colloidal Stability
There are different kinds of forces that explain the interactions in a dispersion of particles in a liquid. There is an electrostatic force that makes the particles repel each other and make the dispersion very stable if they have the same charge. There is also an attractive electrostatic force that strives to get the particles to coagulate. Finally there is an attractive force that exists between neutral particles that can be compared to those between neutral molecules. This is called dispersion forces, or van Der Waal forces, and is caused by a transient dipole moment. This transient dipole moment origin in a fluctuation in the electron cloud of a molecule and will result in a chain reaction of induced dipole moments in neighboring molecules.

If a system is to be considered electrostatic stabilized or not is due to the total interactions between the particles. If the repulsive forces are strong enough, an energy barrier appears when the particles approach each other. If the barrier is too high for the attractive forces to take over, the system is considered stable. If the barrier is sufficiently low so the particles can
get very near each other, the attractive forces takes over and the system coagulates. How quickly this happens is due to the collision frequency and of the probability that the repulsive barrier can be overcome. Collisions can be caused by diffusion (Brownian motion) and by stirring (shearing). If the particles are <1 µm the reason for colliding is mainly by diffusion, but are they larger as for flocculation of fibers the collisions depend mostly on stirring.

Particles can adopt charge in different ways. The dissociation of carboxylic acid groups gives fibers their charge. Particles can adopt a charge by adsorbing ions of different charge from the solution. This will influence the distribution of ions in the solution. Near a positive charged surface there is a higher concentration of negative ions than out in the solution and the opposite for a negatively charged surface, figure 2. This will create a potential $\phi$ relative the solution; this layer is called the electrical double layer.

![Figure 2: Near a positive charged surface there is a higher concentration of negative ions than out in the solution. This layer is called the electrical double layer.](http://en.wikipedia.org/wiki/Electrical_double_layer)

The potential can be calculated from Poisson-Boltzmann’s equation [Appendix 1]:

$$\frac{d^2 \phi}{(dx)^2} = -\varepsilon_0 (C_+ + (x) - C_- - (x)) / (\varepsilon_0 \varepsilon_0 0)$$

Solving this equation for $\phi(x)<25\text{mV}$:

$$\phi(x) = \phi(0)e^{-\kappa x}$$

where

$$\kappa^{-1} = \frac{\varepsilon_0 kT}{\sqrt{2N_A e^2 f}}$$

$\kappa^{-1}$ has the dimension of length and is called the Debye-length. It is the distance from the surface at which the potential has fallen to $1/e = 0.37$ of the potential at the surface. It can be taken as a measure of how far out in the solution the particle charge has effect.

Some systems, where the electrostatic repulsion is negligible, are stable anyway. The particles are covered with a layer of adsorbed polymers. When particles with polymer layers approach each other the concentration of polymers gets higher between the particles and the osmotic repulsion holds them apart. Also, the polymer has access to fewer conformations and this is not entropically favorable. Another reason is that the polymers prefer to interact with the molecules of the solvent and will be surrounded by them instead of other polymers. [4, 8]
2.3 Paper Chemicals

There are different kinds of paper chemicals. To obtain certain qualities for the final paper product, strength in wet and dry state for example, performance chemicals are added. Other paper chemicals are retention aids and biocides, process chemicals, which facilitate the manufacturing process.

Figure 3 shows a wire-cloth opening with fibers and fillers. The fillers would pass through the wire-cloth opening if mechanical filtering mechanisms were the only cause of retention. The addition of retention aids helps the attachment of filler and fines to fibers.

![Figure 3](image)

**Figure 3:** The picture shows a wire-cloth opening with the dimension 200 x 200 μm and the fillers up in the right corner are <10 μm. The fiber that covers some part of the opening is about 3000 x 30 μm. [4]

Water-soluble high molecular polymers are often used as retention aids and the most common way they attach the fines to fibers is by bridge formation. They adsorb to one particle and then collide with another and form a bridge between the two particles, figure 4.

![Figure 4](image)

**Figure 4:** Flocculation by bridge formation; a high molecular polymer adsorb to a particle and then collides with another particle, forming a bridge between the particles.

The polymer has to get enough anchoring point on each particle and be sufficiently stretched to be able to overcome the distance between the particles. This has to do with its shape and charge in the solution. A highly charged polymer is more extended because the charges repel each other, see figure 5.
Figure 5: A neutral polymer takes the form of a sphere while a more extended polymer is highly charged and is stretched out because the charges repel each other.

The salt level in a solution is also a factor for the shape of the polymer. If there is a high salinity it reduces the thickness of the electrical double layer. If the distance between the charges on the polymer is larger than the thickness of the double layer, it behaves as if it was neutral and takes the shape of a sphere, see figure 6.

Figure 6: High salinity reduces the electrical double layer; if its thickness is less than the distance between the charged groups of the polymer, the polymer behaves as if it was neutral and will take the shape of a sphere.

The charge and available space on the fiber is also important for the attachment of the polymer to the fiber. The pores in the fiber provide most of the surface and these are opened when the salinity is high; the fibers swell. But if the salt level is too high it reduces the electrical double layer of the polymer and the attraction between the polymer and fiber will decrease. The tendency of the fibers to swell also depends on pH, because of the dissociation of the carboxylic acid groups on hemicelluloses. When the fibers are charged and the carboxylic acid groups are dissociated, the fiber wall swells. This characteristic gives strong and well-consolidated sheets and the fibers respond well to grinding. [4, 5, 8]
2.4 Fluorescence Microscopy

Fluorescence is named from the mineral fluorite, composed of calcium fluoride and exhibits this phenomenon. Not all molecules can exhibit fluorescence, because they have to have a certain structure that makes the molecule fluoresce and this can be detected in a fluorescence microscope. By attaching a molecule that fluoresce, a fluorophore, to a molecule that does not have this quality it is possible to study it in a fluorescence microscope. Two different molecules are used in this study; N-Methylisatoic anhydride and fluorescein-5-thiosemicarbazide.

2.4.1 Fluorescence

Fluorescence is a process in which an atom or a molecule is first excited by absorbing a light quantum (a photon). At excitation the atom or molecule is at a higher energy level. Then there is a partial vibration relaxation because of an internal transformation to a state with lower energy. Then the atom or molecule emits the rest of the energy in the form of light with longer wavelength (lower energy) than the absorbed light to return to its ground state.

![Jablonski diagram showing excitation and fluorescence](image)

**Figure 7**: A Jablonski diagram that shows the excitation of an electron when it adsorbs energy followed by a partial vibration relaxation. Then the curved arrow shows the fluorescence that is emitted when the electron goes back to its ground state.

The substances that exhibit fluorescence are particularly those containing conjugated double bonds or aromatic structures, as well as those that have a rigid structure and then have no opportunity to relax completely through vibration. Fluorescence increases in general with an increasing number of double bonds or aromatic rings. [9]

2.4.2 Fluorescence Microscope

In a fluorescence microscope, the sample is excited with short-wavelength light, such as ultraviolet or blue light. Some of the light is absorbed by the sample and emitted as fluorescence. Despite the strong illumination, fluorescence is relatively weak. To make it possible to view, the use of a second filter is needed, where the light used for excitation is blocked. This filter is placed between the sample and the eye. This filter must be completely opaque to the excited wavelength and completely transparent to longer wavelengths as fluorescence radiation. A fluorescence microscope differs from a microscope used for conventional absorption microscopy on two points, the need of a special light source and two
additional filters. The optical system for a fluorescence microscope consists of two parts, illumination system - from the lamp to the sample including excitation, high pass, filter and observation system - from sample to the eye or camera, including a barrier, low pass, filter. In the illumination system, light is generated from a radiation source. The lamp has to be a powerful source of light and provide plenty of light of short wavelengths. Mercury lamps are the most common because they provide strong emission lines. The light is collected by a collector lens in the lamp housing and focused through a diaphragm to the condenser. The condenser in turn focuses the light to the sample. The excitation filter selects suitable wavelengths of excitations. Usually there is also a mirror behind the lamp, which reflects the light forward to the collector lens. This is an approximate doubling of the amount of light that can be used for excitations. The observation system consists of a lens, an eyepiece and other intermediate lenses between the lens and eyepiece. The lens produces an inverted image of the sample in the plane of visual diaphragm. This image is then magnified through the eyepiece, producing a visible image that can then be examined with the eye or a camera. Between the lens and eyepiece is a barrier filter, which filters out light from the excitation. [10, 11, 12]

2.4.3 Labeling the fines

In order to detect fines in a fluorescence microscope, it is necessary to get them to fluoresce. The bleached kraft pulp fines have no fluorescent properties and therefore it is necessary to bind a fluorescent molecule to the fines in question. It can be difficult to find a suitable fluorophore which binds covalently to the cellulose. The fluorophores that has been used in this study are N-Methylisatoic anhydride and fluorescein-5-thiosemicarbazide. N-Methylisatoic anhydride, also known as MIA, reacts directly with hydroxyl groups on the cellulose chain [13]. To be able to use fluorescein-5-thiosemicarbazide the chains must first be oxidized [14, 15] because then we get reactive groups like aldehydes and ketones in the chain [16]. The bleached kraft pulp fines are already oxidized to some extent. The methods used in this study are simple and straight forward.
2.4.4 Structure and Mechanisms

The molecular structure of the fluorophores N-methylisatoic anhydride (MIA) and fluorescein-5-thiosemicarbazide are shown below.

![Methylisatoic Anhydride](image1.png)

![Fluorescein-5-Thiosemicarbazide](image2.png)

**Figure 8:** The pictures show the structure of the fluorophores; a N-methylisatoic anhydride and b fluorescein-5-thiosemicarbazide.

The reaction of MIA with an alcohol, in this case cellulose, will produce a blue-fluorescent N-methylanthraniloyl (MANT) ester.

![Reaction of MIA with Alcohol](image3.png)

**Figure 9:** Reaction of N-methylisatoic anhydride (MIA) with an alcohol to produce a blue-fluorescent N-methylanthraniloyl (MANT) ester.

Labeling with fluorescein-5-thiosemicarbazide requires oxidized chains [14, 15] because then we get reactive groups like aldehydes and ketones in the chain [16]. The fines that have been labeled are from bleached, mechanically treated pulp and therefore are oxidized to some extent. The reaction shows a general hydrazide where $R^3$ is the structural part that specifies fluorescein-5-thiosemicarbazide.

![General Hydrazide Reaction](image4.png)

**Figure 10:** Reaction of a general hydrazide with a ketone.
2.4.5 Fluorescence Microscopy and Paper Chemistry

There are only a few articles concerning fluorescence microscopy applied to paper chemistry. Keywords such as “fluorescence”, “paper chemistry” and “fines” resulted only in a few relevant articles. The most interesting article in the field was “Visualizing flocculation and adsorption processes in papermaking using fluorescence microscopy” that related to fluorescence microscopy and the interactions between different additives in the suspension. To extend the search of interesting articles a citation map was established to see if more information related to this article could be found.

![Citation Map]

**Figure 11**: Citation map of the article “Visualizing flocculation and adsorption processes in papermaking using fluorescence microscopy” denoted “1. Whipple”.

The articles of Ghimici [17], Tallarek [18], Kalyazina [19], Razdan [20], Xiao [21] and Menkhaus [22] are not relevant to this study and will not be included. The article by Shen [23] is about papermaking grade fillers and how to modify them and even if it is about papermaking it does not touch the subject of this study.

The relevant articles in the citation map are 1-6 and they are summarized below. Article 1 and 2 are quite similar because they are written by the same authors and have similar topics. Further search resulted in two more articles, 7-8, and no citation map could be established because no articles had referred to them.
1. Whipple

**Title:** Visualizing flocculation and adsorption processes in papermaking using fluorescence microscopy

**Topic:** In this study the adsorption characteristics of a fluorescent cationic polymer, a flocculent, were examined using three different slurries; clean fibers, synthetic alkaline furnish and synthetic acid furnish with and without starch and alum. The processes were studied with fluorescence microscopy.

**Result:** When looking at a clean fiber, it appears that the concentration of polymer is greatest on the fibrils, the greater surface area for adsorption. This area is believed to be more receptive to chemical additives and fiber bonding which were confirmed here. At alkaline pH, (normally used in papermaking), the fibrils extend outward to great distances because of the carboxylate groups and this exposes more surface area for the cationic polymer to interact with.

In the synthetic alkaline furnish with CaCO$_3$ filler there is a competition for the high surface areas and the study shows that the cationic polymer is preferentially adsorbed to the CaCO$_3$ filler, one explanation is that the filler particles can adsorb a larger amount of polymer in comparison to the fibrils. The CaCO$_3$ filler are then adsorbed to the fibrils.

In synthetic acid furnish, there is a lower concentration of fines and this gives a lower surface area. Without starch and alum, the polymer adsorbs mostly on the fibrils and when these are added the polymer adsorbs mostly on the fiber surface. Alum can have a determining role in this because earlier studies show that aluminum ions are strongly attached to fibers and influence the subsequent adsorption of polyelectrolytes. Another explanation can be that the additives compete with the polymer and force the polymer to adsorb on the fiber surface instead. [24]

2. Whipple

**Title:** Adsorption of cationic flocculants to paper slurries

**Topic:** In this study the adsorption characteristics of a fluorescent cationic polymer, a flocculent, were examined using three different slurries; clean fiber, a synthetic alkaline furnish and a thermo mechanical furnish with and without dissolved and colloidal substances (DCS). The processes were studied with a fluorescence microscopy.

**Result:** The results are the same as in article 1 for the slurries of clean fiber and synthetic alkaline furnish.

Furnish that contain mechanical pulp is difficult to study due to the large amount of fines and DCS. The results are from a clean, free DCS and slurry with DCS. In the clean furnish, the polymers are adsorbed on the fibrils and as in the first result the concentration is highest at the highest surface areas of the fibrils. When looking at the slurry with DCS, some of the polymer was found on the fibrils but most of it was found in a polymer-DCS complex that looked
insoluble. Different concentrations of DCS were used and it showed that at higher concentrations of DCS the polymer adsorption decreased on the fibrils and more polymer-DCS complexes were induced. [25]

3. Antunes

*Title:* Use of new branched cationic polyacrylamides to improve retention and drainage in papermaking

*Topic:* Branched C-PAM (cationic polyacrylamide) exhibits better retention efficiency than a linear polymer in microparticulate systems according to earlier studies. Here, the branched C-PAM was studied in a single component system. Six different C-PAMs of high molecular weight with different charge density and degree of branching were used to flocculate the suspension. By using a light diffraction scattering (LDS) technique, the following flocculation results were obtained; flocculation kinetics, flocs size and flocs structure.

*Result:* Studies show that charge density and the number of branches per molecule affect the drainage and the retention performance. At low flocculent dosage and contact time, a polymer with medium charge density offers low drainage times and high filler retentions. This in comparison with linear polymers that increases the drainage time and the reason is the more compact structure of the small flocs while the branched polymer forms small flocs with a more open structure.[26]

4. Liimatainen

*Title:* Fibre floc morphology and dewaterability of a pulp suspension: role of flocculation kinetics and characteristics of flocculation agents

*Topic:* The factors that contribute to fiber flocculation are of great interest because the morphology of these flocs affects the dewaterability of a pulp suspension. To gain a better understanding of the dewatering, the aim in this study was to see how flocculation agents and flocculation kinetics affect the morphology of a fibre floc. Floc size, mass fractal dimension, floc strength and the kinetic constant of flocculation was determined by using a digital image analysis system. Cationic polyacrylamides were used as flocculants and NaCl as a coagulant.

*Result:* The key factor that determines the morphology of the fibre flocs is the high bonding ability of the flocculation agent. It determines the floc density and size. The kinetics did not appear to be a key factor. A flocculation agent with high molecular weight, low charge density and having high fiber-to-polymer bonding strength makes the formation of flocs larger and denser than a flocculation agent with low molecular weight and high charge density. When the floc formations are compact, large voids appear around the dense flocs and promote the dewaterability in the fiber suspension. [27]
5. **Ravnjak**

**Title:** Flocculation of pulp fractions induced by fluorescently-labeled PDADMAC  

**Topic:** The goal was to quantitatively describe the adsorption behavior of a polymer, PDADMAC. Flocculation was observed with a focused beam reflectance measurement device (FBRM) that obtained the cord length distribution. By measuring the fluorescently-labeled polymer concentration with a fluorescence detection system in the filtrate, the polymer retention was determined. PDADMAC was added to four different fractions: pulp with GCC (ground calcium carbonate), fines with GCC, fines and GCC.

**Result:** The efficiency of the interaction between fillers and polymer is reduced when fines and fibers are present. This causes poorer floc formation and unstable flocs. Flattening of the PDADMAC chain when it is adsorbed onto the fibers and fines are one reason and another is the competition for polymer adsorption. When fibers were present, fillers (GCC) would attach to them but detach after a while although the polymer would remain on the fiber. PDADMAC does not affect the formation negatively because of the non-producing fiber flocculation and therefore the retention for fillers will be limited. But PDADMAC could be an aid for filler preflocculation because of the stable flocs it formed with GCC when no fines or fibers were present. [28]

6. **Zakrajsek**

**Title:** Influence if cationic starch adsorption on fiber flocculation  

**Topic:** How cationic starch effects flocculation were the focus in this study. The adsorption of cationic starch, shear forces and different concentrations of inorganic salts are parameters that were varied. This was observed with a FBRM probe. The cationic starch binds to fibers through their free hydroxyl groups to the fibers acidic groups. This strengthens the bond between the fibers. [29]

**Result:** “Maximum retention (>90%) was obtained by the addition of 10 mg/g cationic starch and remained constant until 30 mg/g.” [29] But further addition decreased the retention probably because the electrostatic repulsion increases between the molecules.

7. **Chen**

**Title:** Importance of cellulosic fines relative to the dewatering rates of fiber suspensions  

**Topic:** This study evaluated how fines of different sizes affected the gravity dewatering rates. Two sources of fines were used and they came from primary and secondary fines of hardwood kraft pulp and fractions of fines from chemi-thermo-mechanical pulp. The total amount of cellulosic material was constant while the amount of fines was varied. Finally, the water retention was calculated. The whole process can be read in the article.

**Result:** Dewatering rate affected by kraft pulp fines: The result showed that the secondary fines with a more slender shape has a greater effect on the water retention than the primary fines that have a more compact shape. This can be reasoned as fines with a more slender
shape are more flexible, have a larger external surface area per unit mass and this makes them more efficient to block channels in the structure.

Dewatering rate affected by fines from chemi-thermo-mechanical pulp: The results in this test support the conclusion above, here the use of three different size classes, that the smaller the fines are the better it holds the water. They are able to “migrate through the fiber mat and get stuck in positions where they have relatively large effects on mat permeability.” [30]

8. Scharcanski

Title: Simulating colloidal thickening: virtual papermaking

Topic: This is a computer simulation that studies the aggregation and disaggregation of fibers and fines where different parameters are considered. The process is represented in one dimension because of the computational complexity when two- or three-dimensional are studied. Some of the parameters are: “fiber and fine tendency to disperse in the fluid medium, the decaying turbulence on the forming fabric, and the tendency of fibers in the suspension to concentrate around drainage vortices when fluid is being drained from the suspension.” [31] The simulation consists of two steps that are described in the article as fiber-fine mixture specification and fiber-fine dynamical interaction. The article explains this in more detail.

Result: Because of the thrifty data from commercial samples, it is difficult to get the actual parameter settings. And in the environment for the simulation the conditions are easily controlled, but this is difficult with real-world formers. The consequence is that the results complement the thrifty data obtained from commercial samples. To get more realistic results, “one thousand simulated samples were generated, given different forming conditions and fines content.” [31] The results show that when the fines content is increased the fiber flocculation tends to decrease. This supports a hypothesis that “fines tend to stick to fibers, acting as a buffer to fiber-to-fiber interaction and entanglement.” [31]
3. Experimental
The experiments were performed at Karlstad University, department of chemistry and biomedical sciences. The purpose of the experiments was to carry out and evaluate two methods of labeling the bleached kraft pulp fines.

3.1 Equipment and Chemicals

Microscopes:
- Leica DMI6000B
- Zeiss Axioskop2 MOT microscope; HBO100 light source, LC Epiplan 50×/0.5 objective. The digital camera was an ORCA-ER and the image analysis software was Aqua Cosmos Version 2.6, both from Hamamatsu.

Fluorophores:
- N-methylisatoic anhydride Cat. No. M-25
- Fluorescein-5-thiosemicarbazide Cat. No. F-121

Both fluorophores were ordered from Invitrogen

Other equipment and chemicals:
- Sodium Borate
- DMSO
- DMF
- NaOH
- dH2O
- 2-propanol
- Bleached kraft pulp fines prepared at Stora Enso RCK
- Standard equipment in a laboratory

3.2 Method
The following methods were used for the two fluorophores:

MIA: 10 g 2-% mass of fines were mixed with 10 ml of 0.1 M sodium borate (pH 8). 20 ml of DMSO were added. The final concentration of fines was 5 mg/ml. The fluorophore was solved in DMSO so that its final concentration was about 10 mg/ml, 3.6 mg MIA to 360 μl DMSO. The ratio is about 20 μmole fluorophore to 5 mg fines [32]. The fluorophore solution was added directly to the solution with fines and incubated at room temperature for 10 min. 80 ml of 2-propanol was then added so the labeled fines would precipitate and could be filtered by suction. The precipitate was washed with 2-propanol and finally with distilled water. The precipitate were diluted about 10 times and then studied with a fluorescence microscope at the emission wavelength 446 nm.
**Fluorescein-5-thiosemicarbazide**: 10 g 2-% mass of fines were mixed with 10 ml of 0.1 M sodium borate (pH 8). 20 ml of DMSO were added. The final concentration of fines was 5 mg/ml. The fluorophore was solved in DMSO so that its final concentration was about 10 mg/ml, 9.0 mg fluorescein-5-thiosemicarbazide to 900 μl DMSO. The ratio is about 20 μmole fluorophore to 5 mg fines [32]. The fluorophore solution was added directly to the solution with fines and incubated at room temperature overnight on the shaker [33]. 80 ml of 2-propanol was then added so the labeled fines would precipitate and could be filtered by suction. The precipitate was washed with 2-propanol and finally with distilled water. The precipitate were diluted about 10 times and then studied with a fluorescence microscope at the emission wavelength 516 nm.

**4. Result and Discussion**

Two solutions prepared as described in Method were examined in two different microscopes. Fines labeled with MIA was examined in a Leica microscope and fines labeled with fluorescein-5-thiosemicarbazide with a Zeiss Axioskop2 MOT microscope. Both solutions exhibited fluorescence but the fines were mostly aggregated. This must have happened when the different components were mixed together, so no particularly movements were noticed. The aim of this experiment was to show if the labeling was a success therefore the concentrations were not established.
4.1 Results for fines labeled with MIA
The fines labeled with MIA were studied with a black and white camera. The pictures are blue due to pseudo colouring, as they appear in real-life. Figure 12 show the fines labeled with MIA.

![Image]

**Figure 12:** To the left: one fine with length 500 µm approximately. To the right: an appropriate concentration (unknown) so the fines were easily seen in the microscope.

4.2 Results for fines labeled with fluorescein-5-thiosemicarbazide
Figure 13 show the fines labeled with fluorescein-5-thiosemicarbazide. The two pictures of the fines labeled with fluorescein-5-thiosemicarbazide are identical but one is shown with normal light, and the other shows the fluorescence.

![Image]

**Figure 13:** Fines labeled with fluorescein-5-thiosemicarbazide. The two pictures are identical. The left image refers to normal light. The right image refers to fluorescence.
4.3 Discussion
The labeling of fines was a success and the fluorescence was easy to detect. The aggregation of fines is negative because the individual trajectories are difficult to study in the aggregated state. The aggregates formed when fines were mixed with DMSO, not their natural environment. The aggregation appears to be irreversible because attempts to disperse the fines by magnetic stirring for a long time did not work. A reason for this is the well-known phenomena, hornification.

5 Conclusion
The study of the interaction of fines with other materials such as fibers in the paper-making process by means of fluorescence microscopy appears to be relatively unexplored. Several articles on fluorescence labeled fibers, retention aids or additives have been found in this study [24-31, 33]. The process of labeling the fines with a fluorophore was straight forward. The result was aggregates of fluorescent labeled fines. The labeling process has to be developed in a way that avoids aggregation; one way might be to use water as a solvent instead of DMSO. The individual trajectories of fines are needed for creating knowledge about the interactions between fines and other components.

6 Future Work
More information must be gathered when it comes to fines so an additional literature study must be done. The process of labeling the fines will be modified to avoid aggregation. The diploma work of Åsa Nyflött [34] provides an image analysis tool for following the trajectories of fines. The thesis by Åsa Nyflött also covers a simulation of Brownian motion. This can be used for understanding the interactions between fines and other components when making paper.

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8 Appendix 1

The potential can be calculated from Poisson's equation:

\[
\frac{d^2 \phi}{dx^2} = -\frac{\rho(x)}{\varepsilon_0 \varepsilon}
\]

\(\rho(x)\) = charge density

\(x\) = distance from the surface

\(\varepsilon_0\) = dielectric constant in vacuum

\(\varepsilon\) = medium relative dielectric constant

When the ions are assumed to distribute according to Boltzmann's law we get an expression for the charge density \(\rho\):

\[
\rho = z\varepsilon(C_1 + (x) - C_1 - (x))
\]

where the following expressions are of a negatively charged surface:

\[
C_+ (x) = C_0 e^{-\frac{ze\phi(x)}{kT}} \text{ concentration of positive ions at the distance } x \text{ from the surface}
\]

\[
C_- (x) = C_0 e^{-\frac{ze\phi(x)}{kT}} \text{ concentration of negative ions at the distance } x \text{ from the surface}
\]

\(C_0\) = concentration in the solution when \(x\) goes to infinity

\(ze\) = charge of ion

\(\phi(x)\) = potential at distance \(x\) from the surface

\(k\) = Boltzmann constant

\(T\) = absolute temperature

If the term above is inserted in Poisson's equation then it is called Poisson-Boltzmann equation. It can be solved using the current boundary conditions and the direct solution is obtained when the surface potential is low (\(\phi (x) < 25\text{mV}\)) is:

\[
\phi(x) = \phi(0)e^{-\kappa x}
\]

where

\[
\kappa^{-1} = \sqrt{\frac{\varepsilon_0 kT}{2N_A e^2 I}}
\]

\(I\) = ionic strength of the electrolyte, and here the unit should be mole/m³

\(N_A\) = Avogadro number

\(e\) = elementary charge
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