# Analysis of pulp components in a DIP process with tube flow fractionation

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## ABSTRACT

The aim of this study was to clarify how the aging of raw material affects the behaviour of paper components in pulping and flotation. The main measurement method in the study was tube flow fractionation which classifies pulp gently according to particle size, and allows gathering separated fractions for microscopy study and image analysis. The study showed that aged raw material has considerably poorer properties in sense of slushing rate. The amount of attached ink particles was higher in case of aged material than fresh material. Also ink removal efficiency in flotation was lower with the aged raw material than fresh material. Due to these two reasons the aged material had lower brightness of pulp than fresh material.

## INTRODUCTION

The age of recovered paper can vary considerably. Previous studies showed that deinkability of aged paper is generally lower /1,2,3,4,5/. The consequence of aging is a reduction in final pulp brightness, due to decreased detachment of ink. It has been suggested that this is due to the oxidation of ink, that bonds ink stronger to fibre material /6/. The oxidation of ink increases with prolonged storage time, especially at elevated temperatures /6/. This is the reason why the mill environment aging or thermal aging phenomenon is noticed usually during the summer period and is called informally as a summer effect.

According to the literature /6,7,8,9,10/, it seems that aging and thermal aging lead to increased ink fragmentation and ink attachment. These studies do not give any detailed information, however, e.g. how much ink exists in each fibre length class and what is the attached ink size distribution. Such fractional approach might give new insight into deinking mechanisms, and would be essential for finding optimal process conditions.

The aim of this study was to clarify with fractional analysis, how the aging of raw material affects the behaviour of paper components in pulping and flotation. The special interest was the detachment and fragmentation of ink, and how ink is distributed among fibre length classes. The fractional measurement method in the study was tube flow fractionation that classifies pulp gently according to particle size, and after that it is possible to gather separated fractions for microscopy study and image analysis. By means of fractional information, it is possible to recognize the amount of free and attached ink as well as ink particle size distribution. Fresh and old raw materials were processed in a DIP pilot plant in similar conditions and pulp samples were collected for further analysis.

The results indicated that additional information (size distribution and amount) about attached and free ink of pulp fractions can be attained with the fractional method.

## MATERIALS & METHODS

### Experimental

Pulp samples were collected from the several process stages of the 1-loop continuous deinking pilot plant at the University of Oulu. A schematic description of the pilot process is illustrated in Figure 1. Descriptions of the sampling points are listed in Table 1. The raw material in these trials had ONP-OMG ratio of 50%-50%. In the first trial, fresh material, i.e. 10 weeks old was used, while in the second trial 30 weeks old aged material was used. The raw material was identical in both trials, only the age was different.

Table 1. Sampling points in the tests.

| Sampling point | Description of the test point |
|---|---|
| Drum pulper | Samples from batch drum pulping |
| Pulper accept tank (PAC) | Pulping samples after dilution |
| Flotation feed (FFE) | Flotation cell feed samples |
| Flotation accept (FAC) | Flotation cell accept samples |
| Flotation reject (FRE) | Flotation cell reject samples |
| Wire press outlet (WPO) (final pulp) | Pilot process product |

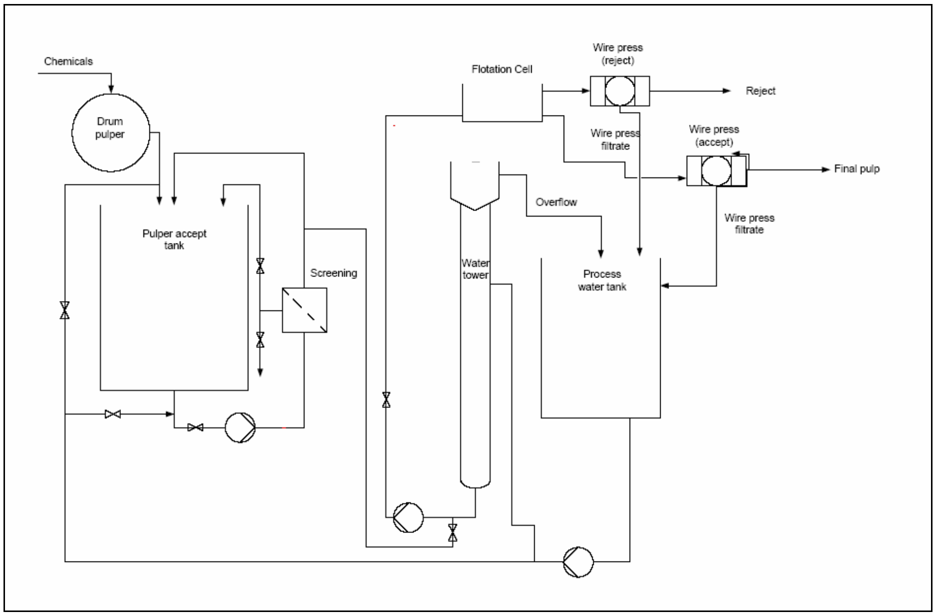


Figure 1. A schematic description of the pilot process.

Before full line process trials, the effect of pulping time was studied with fresh and aged raw material in the pilot drum pulper having a diameter of 2 m. Pulping time varied from 10 to 30 min. The pulping was performed at 16% consistency with conventional alkaline soap chemistry (Table 2). In full line tests, similar conditions were used, but the pulping time was 20 min.

Table 2. Pulping conditions.

| | Pulping performances |
|---|---|
| Raw material | 50% ONP & 50% OMG (central European) |
| Pulping consistency | 16% |
| Pulping temperature | 50°C |
| Pulping batch | 35 kg (air dry) |
| NaOH | 10 [kg/t] |
| Waterglass | 9.3 [kg/t] |
| Commercial fatty acid soap | 6 [kg/t] |
| H2O2 | 10 [kg/t] |
| Hardness [°dH] adj. CaCl2 | 20 [°dH] |

After the drum pulper, the pulp was diluted first to consistency of 2-3%, coarse screened and then fed into a flotation cell at a 1.0% consistency after the second dilution. The delay in the flotation cell was 15 min and the air-pulp ratio was kept above 1.3. During the trials, the mass reject rate of flotation was set to 9-12% by adjusting the surface level in the cell. After flotation, accepted pulp was dewatered by a wire press. Also flotation reject was dewatered and both filtrates were collected to the process water tank and used to the dilutions. Because of the recirculation of the process water, the fresh water consumption was around 4-5 $m^3$ per ton of pulp.

**Analysis**

*Tube flow fractionation*

The tube flow principle has been discussed in several publications /11,12,13,14,15/. In tube flow fractionation (see Fig. 2.), a pulp sample is separated into fractions with a continuous water flow. In the measurement a given amount of pulp (the typical volume is 50 ml and consistency is 0.3%) is injected into the constant water flow through a long plastic tube, which is wound on a wheel. As initially short pulp plug flows through the long tube it spreads and is fractionated by size. The phenomenon is similar to that in chromatography, where molecules are fractionated according to their size. The fractionated plug is then divided into bins, where the first contains the biggest particles and the last contains the smallest ones. Consistency transmitter measures the mass of the pulp in fractions. In this case, the fibre fractions from the first to the fourth bin can be characterised to contain flakes (FR1), long fibres (FR2), short fibres (FR3) and fines/fillers (FR4), respectively. On the other hand, ink particles from the first to the last fraction could be described as dense printing on the flakes (FR1), ink attached to long fibres (FR2), ink attached to short fibres (FR3) and free ink (FR4). /16,17/

The tube flow fractionator separates the whole pulp sample into specified fibre fractions and a fines fraction in about 4 minutes. When conditions (flow rate and water temperature, etc.) during the fractionation procedure are kept constant, the fractionation is very reproducible.

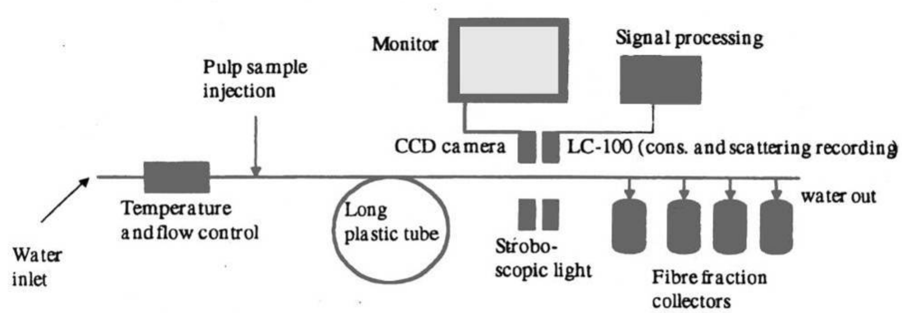


Figure 2. A schematic description of the tube flow fractionator /14/.

Table 3 presents the tube flow fractionator fractions and average particle size of fractions according to FiberLab (Metso Automation), respectively. Each fraction contains of particles very different sizes.

Table 3. Tube flow fractionator litre ranges and them average fibre length.

| Tube flow fractionator | Tube flow fractionator litre ranges | Average fibre length [mm] |
|---|---|---|
| 1. fraction, flakes (FR 1) | 14.80-16.30 | over 4.0 |
| 2. fraction, long fibres (FR 2) | 16.30-17.50 | 1.85 |
| 3. fraction, short fibres (FR 3) | 17.50-18.30 | 0.60 |
| 4. fraction, fines (FR 4) | 18.30-20.30 | 0.18 |

*Dry content and ash content*

Dry content and ash of the same sample were analyzed by evaporating water at 105°C and burning dry sample at the furnace of temperature 525°C (ISO 638 and 1762, respectively).

*Brightness and residual ink*

For each pulp sample standard pulp pads were prepared according to INGEDE Method 1. Pads were analysed with L&W Elrepho spectrophotometer using light wave length of 457 nm for brightness and 700 nm for residual ink. Some of pulp samples were hyperwashed with a 150 mesh wire screen in order to measure attached ink.

*Microscope and image analysis*

A suitable amount of each fraction was filtered out onto membrane filter foils in order to investigate the samples with a microscope. Cellulose ester membrane filters (Schleicher & Schuell, ME 25) were used in this study. The diameter and pore size were 50 mm and 0.45 µm, respectively. It was necessary to ensure that the fraction samples filtered onto the white membrane filter foil did not contain too many particles, to avoid forming more than one layer on the filter foil.

After filtering, the samples were dried at 50°C. A digital camera and microscope (Leica DFC320) were used to study the samples. Each sample was photographed using a constant picture ratio. The transformation ratio from pixel to mm was determined. After that it was possible to handle all the data also on a metric scale.

Sample images were analysed with image analysis software (Matrox Inspector) that calculated the number, length, width and area of dark particles (i.e. ink particles). The threshold value was set manually. Particles in the different size categories were counted on the basis of the image analysis. The smallest particle size visible with the light microscopy used is 3 µm.

## <u>Calculations</u>

Ink reduction or free ink cleanliness efficiency:

$$E_C = \frac{C_F - C_A}{C_F} \cdot 100\%, \qquad (1)$$

where

$E_C$ is the cleanliness efficiency [%]
C is the content of a given component [ppm]
Subscript A refers to the accept
Subscript R refers to the reject
Subscript F refers to the feed

## RESULTS

*Pulp component analysis in pulping and flotation*

Slushing rate of the fresh and aged raw material was compared during the drum pulping and the results are presented in Figure 3. It was observed that aged raw material slushed poorer; flake content (FR1) was about twice as high as in fresh material. With aged material, 30 minutes pulping time was needed to reach the same amount of flakes than fresh material reached after 10 minutes of pulping.

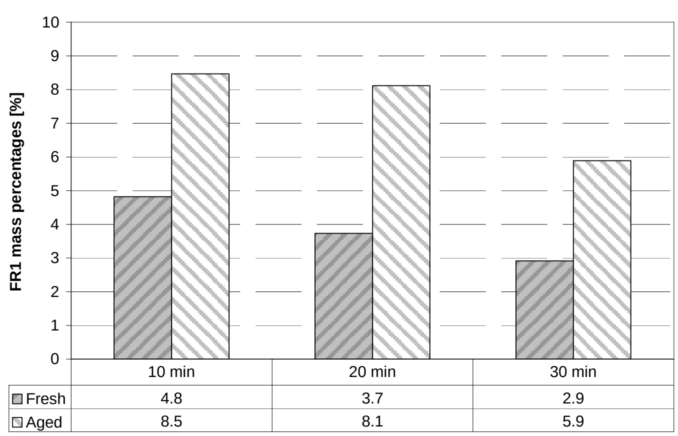


Figure 3. Flake content as a function of pulping time in drum.

Weight proportions of fractions in the various sampling points are shown in Table 4. Even if the flake content differed in the pulper samples, it evened out when pulp was diluted in the pulper accept tank and when pumping and screening took place. There were no considerable differences in the weight proportions of fibre fractions if the same process stages were compared. The ash content was at comparable levels after pulping, but it seemed that the yield of ash in flotation was lower with aged raw material.

Table 4. Weight proportions of the fractions according to the tube flow fractionation method.

| **Fresh pulp** | **Proportion of flakes [%]** | **Proportion of long fibres [%]** | **Proportion of short fibres [%]** | **Proportion of fines [%]** | **Ash content (525°C) [%]*** |
|---|---|---|---|---|---|
| Pulper (20min) | 3.7 | 37.6 | 23.2 | 35.4 | 24.6 |
| PAC | 1.0 | 35.3 | 22.6 | 41.0 | n.a. |
| FFE | 0.3 | 34.1 | 22.3 | 43.2 | 34.7 |
| FAC | 1.7 | 35.9 | 23.0 | 39.4 | 32.7 |
| FRE | 0.3 | 8.7 | 14.2 | 76.7 | 54.9 |
| WPO | 2.6 | 43.7 | 26.4 | 27.3 | 15.9 |
| **Aged pulp** | **Proportion of flakes [%]** | **Proportion of long fibres [%]** | **Proportion of short fibres [%]** | **Proportion of fines [%]** | **Ash content (525°C) [%]*** |
| Pulper (20min) | 8.1 | 37.4 | 22.6 | 31.9 | 24.9 |
| PAC | 1.9 | 39.8 | 23.7 | 34.6 | n.a. |
| FFE | 1.4 | 33.4 | 23.9 | 41.3 | 32.5 |
| FAC | 1.8 | 35.1 | 24.7 | 38.4 | 29.2 |
| FRE | 0.4 | 12.6 | 12.8 | 74.2 | 55.0 |
| WPO | 3.0 | 44.9 | 27.9 | 24.2 | 9.1 |

*ISO 1762

*Residual ink and brightness*

Residual ink values were much higher in aged pulp, which indicated fragmentation of ink particles. After first dilution (PAC), residual ink values were over 500 ppm higher with aged material than in the case of fresh material (Fig. 4a). After flotation, residual ink values were still almost 300 ppm higher with aged material than with fresh material. Ink reduction in the flotation cell was 83% with fresh material and 71% with aged material (equation 1). The hyperwashing results showed that, in the case of aged raw material, there were a lot of attached ink particles in the fibre fractions (Fig. 4b). After hyperwashing, the aged material had 170 ppm higher residual ink value than fresh material.

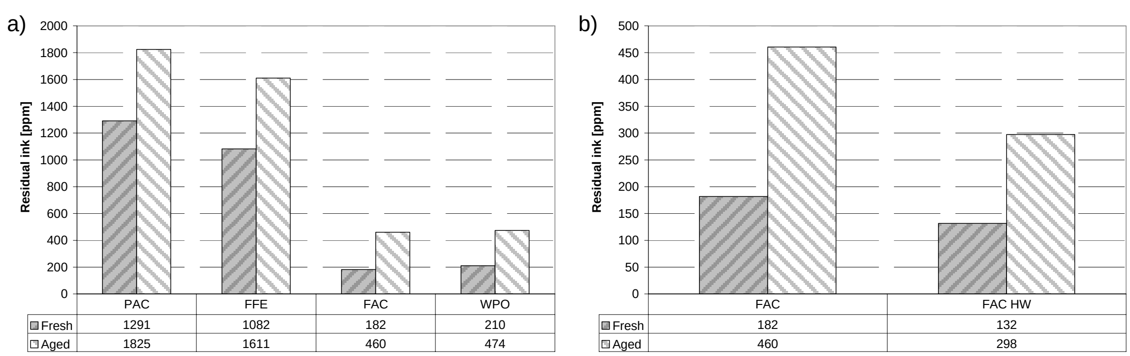


Figure 4. Residual ink values of the pulps in various process stages (a) and hyperwashing results (b).

Free ink cleanliness efficiency in flotation can be calculated with help of hyperwashing results. Hyperwashed values were subtracted from the original values of flotation feed and accept and then these free ink values were compared to each other. Free ink cleanliness efficiency in the flotation cell was 95% with fresh material and 88% with aged material (equation 1).

Because differences in residual ink values between aged and fresh pulps were so significant, it is obvious that differences should have also seen in brightness. Indeed, brightness was 5-8 point higher along the process line with fresh material than with aged material (Fig. 5).

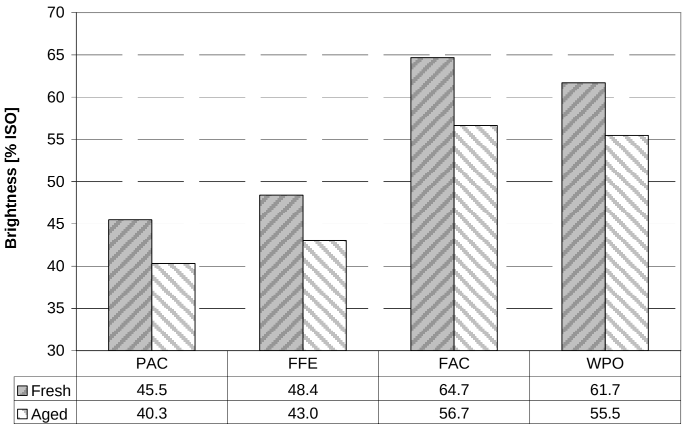


Figure 5. Brightness values of the pulps in various process stages.

*Microscopy analysis*

Filtered samples of fractions 2, 3 and 4 were analysed with the microscope. Microscope pictures of fractions 2, 3 and 4 after 20 minutes drum pulping are presented in the Appendix. These pictures visualize the differences between fresh and aged material. Total area of ink particles in flotation feed samples (a) and in flotation accept samples (b) are plotted in the Figure 6. It is good to notice, that the y-axis is logarithmic.

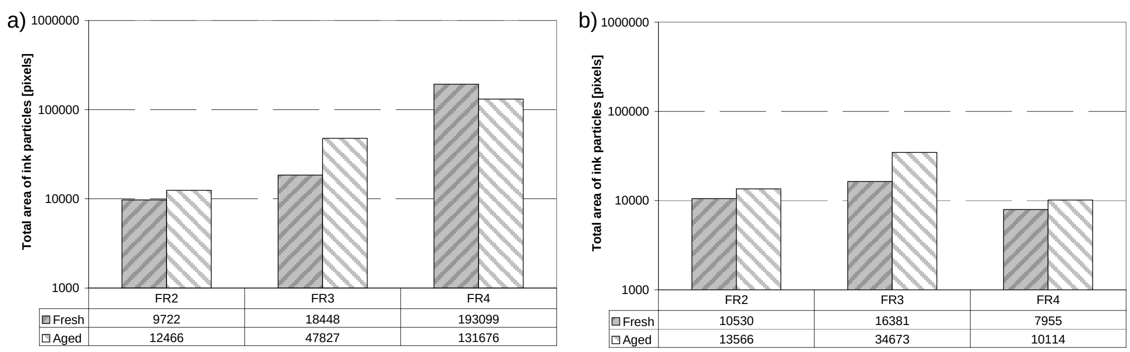


Figure 6. Total area of ink particles flotation feed (a) and flotation accept (b) according to the image analysis.

Floatable free ink was carried along to fraction 4 during fractionation. Free ink can be removed well during flotation with aged and fresh materials, although reduction was a little bit lower with aged material (Table 5). There was some free ink or short fibres were rejected among short fibre fraction, because a small reduction in ink content was seen. The reduction was better for aged pulp, but the amount still remained at higher level after flotation. Among long fibre fractions, there was no free ink found. Attached ink in long and short fibre fractions was higher with aged material, as it can be deduced from Fig. 6b. In fines fraction (FR 4), the ink content is apparently lower than in fibre fractions, however this results is somewhat misleading, because the resolution of the microscope was not enough for particles with size below 3 μm.

Table 5. Ink reduction of the different fractions and whole pulp in pilot flotation.

| Ink reduction [%] | FR2 | FR3 | FR4 | Total |
|---|---|---|---|---|
| Fresh material | ≈ 0 | 11 | 96 | 83 |
| Aged material | ≈ 0 | 28 | 92 | 71 |

The size distribution of ink particles in flotation accepts were analysed in order to understand the differences between fresh and aged material. In fractions 2, 3 and 4, the size distribution for fresh and aged material are plotted in Figures 7-9. Figures 7 and 8 indicate that the amount of attached ink particles were clearly higher in fraction 3 than in fraction 2. In addition, the amount of small ink particles is clearly greater than large ink particles. In practice, there were no free ink particles larger than 50 μm in fraction 4 after the flotation (see Fig. 9).

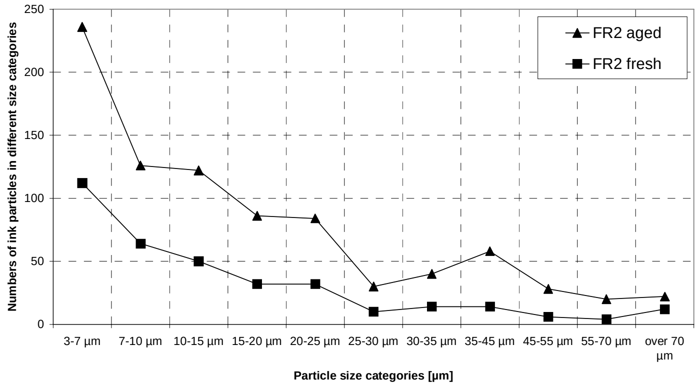


Figure 7. Size distribution of the ink particles in flotation accept with fresh and aged material in fraction 2.

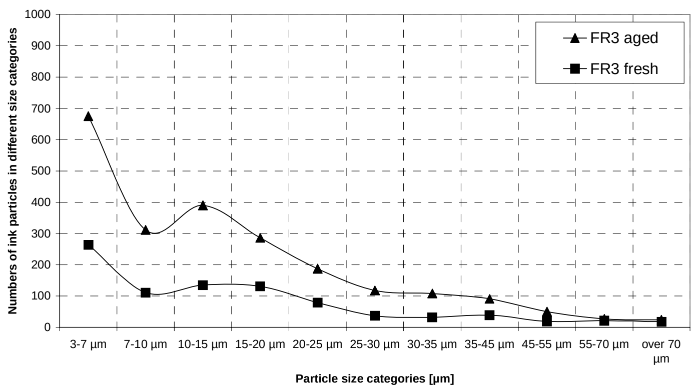


Figure 8. Size distribution of the ink particles in flotation accept with fresh and aged material in fraction 3.

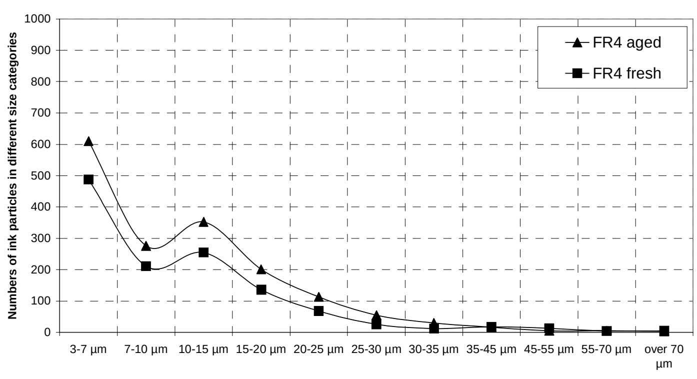


Figure 9. Size distribution of the ink particles in flotation accept with fresh and aged material in fraction 4.

## DISCUSSION

Previous studies on paper aging have usually been performed either in laboratory or mill scale and they both have their disadvantages. In laboratory experiments, process conditions do not correspond to actual mill conditions but, on the other hand, in mill experiments raw material changes during seasons make comparison of results difficult. In our experiments, we used the pilot plant, because pilot scale experiments make it possible to control raw material, and process conditions are more accurately than industrial conditions.

*Pulp component analysis in pulping and flotation*

Aged paper needed more slushing time in drum pulper, in order to diminish the amount of paper flakes at an acceptable level. The effect may be connected to wetting of fibres, which may take more time in case of aged material. In practice, pulping time is constant and, if there is a lot of aged raw material, an additional yield loss is possible if deflakers are not used, because flakes will be rejected in coarse screening. Prolonged pulping time would help, but it is economically not feasible.

Despite of higher amount of flakes in pulper with aged raw material, weight proportions of fibre fractions differ only slightly from fresh raw material after pulping. However, in flotation, ash seems to be rejected more willingly. The reason may be in size distribution of ash that may refer to higher content of coating flakes. It is also possible that more ash is attached to ink than in the case of fresh raw material. More research is needed in order to clarify this observation.

*Residual ink, brightness and microscopy analysis*

Apart of slower slushing rate, aged raw material demonstrate also reduced ink detachment, which could be seen in RI values, brightness as well as microscopy analysis. Highly prolonged slushing time would be needed in order to reach the same level of ink detachment as with fresh raw material. However, the results indicate, that it would lead to a high amount of very fine ink particles difficult to remove in flotation.

Fractional microscopy study showed that ink content in fines fraction in the case of fresh raw material is higher after pulping because of better detachment of ink. Despite of this, the reduction of free ink is better in flotation, indicating more beneficial size distribution. In the case of aged raw material, very fine ink is produced and it is difficult to remove in flotation. As mentioned earlier, the finest material (below 3 μm), which might be responsible for lower removal efficiency in flotation, could not be measured optically. Size distribution of ink measured by microscopy was quite similar after flotation, but the ink content was substantially higher for aged raw material in each size class. A higher amount of ink in largest size classes leads inevitably to a higher amount of dirt specks in aged raw material.

Fractional analysis showed long fibres to be the cleanest fraction, with respect of attached ink. Ink attachment is clearly higher in short fibre fraction, while almost all free ink is in the fines fraction.

It would be useful to measure ink content separately from fibre fractions and fines fraction from DIP process online, because it provided information on attachment and floatability or washability of ink in pulp. Such measurement would offer new possibilities to control pulp quality in various process stages; pulping, flotation, dispersion and bleaching. Online measurement of these properties of pulp is possible to develop based on a tube flow fractionator.

## CONCLUSIONS

The fractional study with the tube flow fractionation method shows that aged raw material has considerably poorer properties in sense of slushing rate, which may lead to lower yield if paper flakes will be rejected in coarse screening as well as to ink detachment causing lower brightness of pulp. The amount of attached ink particles is higher in short fibre fractions than in long fibre fraction. Due to smaller free ink particles in case of aged raw material, reduced ink removal efficiency in flotation is attained.


## ACKNOWLEDGEMENT

The authors wish to thank T. Huhtelin (Metso Automation) and T. Hannuksela (Kemira) their technical assistance in this manuscript and Metso Automation for their support of this research work.

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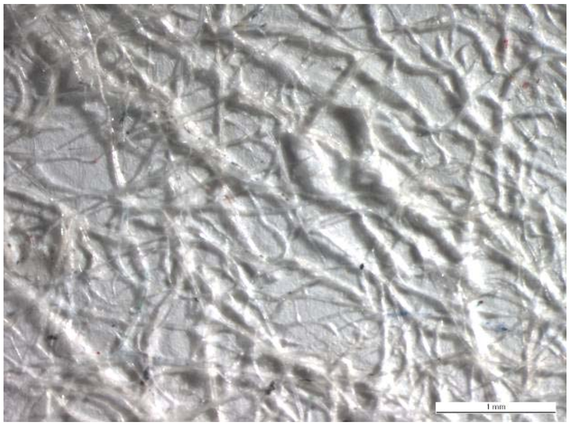
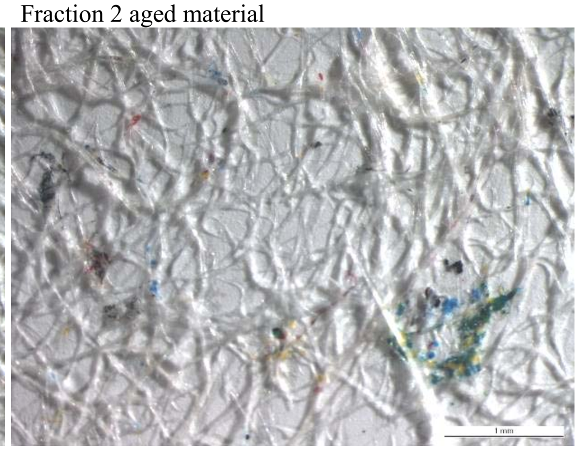
# Appendix

Fraction 2 fresh material



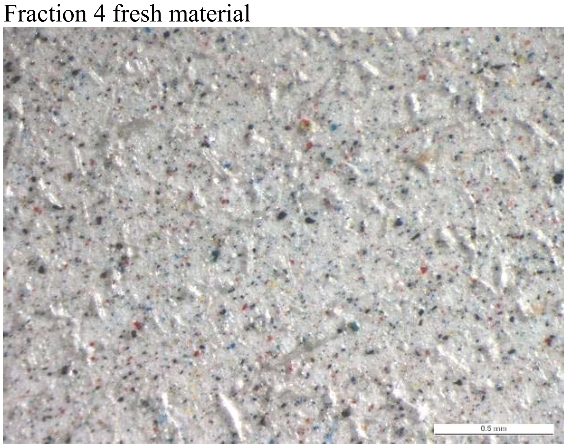

Fraction 2 aged material




Fraction 3 fresh material


Fraction 3 aged material


Fraction 4 fresh material




Fraction 4 aged material