HYDROGEN PEROXIDE AND RELATED CHEMICAL ADDITIVES IN DEINKING PROCESSES

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ABSTRACT

The increasing requirement for high quality printing paper consisting partially or entirely of secondary fibers, along with environmental pressure to use as low levels of chemicals as possible, have motivated a search for the optimum use of chemicals in a deinking line. An examination was made of the role of each chemical in the different stages of the deinking processes. A clear distinction was drawn between pulping chemistry and bleaching chemistry; i.e., although some chemicals are used in both pulping and post-bleaching, their effects on the operation in question can be totally different. In particular, the optimum point of introduction of hydrogen peroxide was investigated. Special attention was given to the interaction between the chemicals and to the different actions of the chemicals in the presence and in the absence of ink.

In addition to studies of deinking chemistry, work was done on the refinement of measurement techniques used for the evaluation of different aspects of recycling.

1. INTRODUCTION

Three waste paper recycling operations in which the chemistry has an important role are pulping, flotation and post-bleaching. The attention given to each of these operations depends on the final paper quality wanted.

The first operation is pulping. In this stage the dry paper stock is disintegrated. This stage determines the efficiency of subsequent stages since the size of the contaminants and their bonding with the cellulose fibers is determined during pulping.

The second recycling stage with an important chemistry, is the separation of useful material (such as fibers and in some cases a part of the filler material) from impurities (such as solid material, adhesives and ink particles). In general, two techniques are applied for this purpose: washing or flotation. Deinking mills can use one of these techniques, or a combination.

For some applications demanding high brightness recycled paper, a third step can be included in the deinking line: the purified fibers can be bleached. This can be done in a one or two stage post-bleaching, sometimes in combination with a mechanical treatment (disperger). With a mixed furnish of newspapers and magazines, the bleaching stage has some similarity to mechanical pulp bleaching. However, most of the recycled fibers have been bleached before and so they will not necessarily respond in the same way to the bleaching stage.

The aim of this study is to explain the role of hydrogen peroxide and related chemicals applied in one or several of the recycling stages described before. Most of our attention was given to pulping chemistry and to post-bleaching.

In this study, a flotation was carried out between pulping and post-bleaching to separate the ink from the fibers. Other cleaning or screening stages were not included in this study since the furnish used was an artificial mixture with only newspapers and magazines (no envelopes, adress labels, wires, etc.). Given the limitations of any laboratory scale deinking study, our objective was a qualitative rather than a quantitative definition of the actions of various chemicals.

Special attention was given to the measurement techniques used to separately evaluate the brightness gain obtained by deinking and the gain obtained by bleaching.

2. EXPERIMENTAL PROCEDURE

2.1. Furnish

Trials were done with a 50/50 mixture of newsprint (Le Soir) and magazines (Cine Revue). The newsprint paper consisted partially of recycled fiber. The printing process for the newspapers was letterpress; for the magazines it was gravure. The age of the newspapers and the magazines was less than three months, in order to avoid variability from aged furnishes.

2.2. Process Simulation

A Lamort laboratory pulper with 18 kg content was used. The operation temperature, time and consistency were fixed at respectively 50 °C, 30 minutes and 11%. The addition levels of caustic soda, sodium silicate and hydrogen peroxide were varied as presented in table 1.

	pulper	post-bleach
NaOH	0 - 3%	0 - 3%
NaSi	0 - 5%	0 - 5%
H2O2	0 - 2%	0 - 4%

TABLE 1: Chemical addition levels

Caustic soda and hydrogen peroxide levels are given as the percentage applied on dry pulp (o.d.p.) of 100% reagent. Sodium silicate is used on a solution basis (waterglass; 38 Bé). Its contribution to the total alkalinity is equal to 0.112% of the silicate level used.

To simulate a flotation stage, a Voith laboratory flotation cell was used. A "hyperflotation" was made to ensure that all ink particles which could be eliminated by flotation would be eliminated. The flotation cell was operated for 20 minutes at 40 °C and 0.8 % consistency. For all trials, the pH was adjusted to 9 before flotation, unless specified otherwise.

As a surfactant for flotation, 1% sodium stearate was added to the pulper. The working mechanism of this surfactant is based on calcium soap formation. Therefore, the water hardness of the process water was adjusted to 10 °dH, unless specified otherwise. This artificial hard water was prepared by adding calcium chloride to demineralised water.

Post bleaching trials were performed at 25% consistency in polyethylene bags placed in a warm water bath for 1 hour. The temperature was kept constant at 70 °C. For this purpose the pulp was preheated at 90 °C. The variations in the chemical addition levels are also given in table 1.

2.3. Measurements

Optical properties were measured on brightness pads with a basis weight of 50 g/m^2. To eleminate the influence of the pulp pH on brightness measurements, all samples were acidified to pH 5 with sulfuric acid before the brightness pads were prepared. To avoid the large and negative influence of ink particles, optical properties are measured after flotation.

All brightnesses are expressed as brightness gain. The initial brightness is measured after the pulper without caustic soda, sodium silicate or hydrogen peroxide.

MILLIPORE$^{(R)}$ filters with 8 µm pores were prepared for image analysis (see further). A separate section is dedicated to the development of the image analysis method.

3. IMAGE ANALYSIS

A combination of several measurement techniques is necessary to evaluate appropriately the effectiveness of the deinking process (1).

Brightness measurements can only have limited value in evaluating deinking efficiency since brightness gives only an overall result. No difference can be determined between the effect of the chemicals on ink removal and the bleaching effect on the fibers.

Therefore, a second measurement technique, image analysis, was used in this study. Ink particle size distributions and the percentage of the sample covered by ink particles were determined. The efficiency of ink removal by flotation is related to the size of the ink particles (2). With the aid of image analysis, a relationship was found between the chemical composition of the pulping liquor and ink particles size distribution after pulping. This was used to establish the role of some chemicals in the pulper.

In this study, ink particles were measured using a QUANTIMET$^{(R)}$ 970 image analyser (Cambridge Instruments) on samples prepared after pulping . The percentage of the measured sample area covered by ink and ink particle size distribution histograms are given by this technique. In the size distribution histograms, the ink particles are distributed in 4 size classes (10-30 µm, 30-50 µm, 50-70 µm, > 70 µm).

3.1. Sample preparation

Sample preparation is a very important factor for valid image analysis results (3-5).

The following precautions were taken:

1. MILLIPORE filters were used to ensure that no ink particles were washed out during sample preparation. The dimension of the filter pores were chosen in relation with the size of the ink particles to be counted.

2. The amount of pulp deposited on the filters is a compromise between different considerations. The more pulp, the higher the number of ink particles and the more accurate the size distributions. On the other hand, the amount of pulp has to be limited in order to obtain a smooth surface, necessary for a well focused image when microscopic magnifications are used. Also, to avoid ink particles being covered by fibers and to minimize the number of overlapping fibers, the amount of pulp on each filter has to be small.

The following method gives thin and smooth samples without too many overlapping fibers:

A thin layer (10 g/m^2) of pulp is deposited on a microfilter with 8 µm pores. The sample is not removed from the filter before examination.

3.2. Analysis procedure

The area of the sample to be examined depends on:

- the number and dimension of the ink particles in the sample
- the homogenity of the sample

and determines:

- the precision and reproducibility of the obtained results
- the time and cost of the analysis

We found that at least 30 particles have to be counted in each size class to obtain an acceptable reproducibility (relative standard deviation < 15%) of the size distribution. When series of trials are being compared, this number can be lowered. The microscopic magnification has to be chosen so that each ink particles covers at least 60 pixels on the video screen of the analyser. This to reduce border effects in surface calculations.

A standard deviation of 10% was found on the number of particles in each class and on the percentage of surface covered by ink.

Image analysis, as described before, was applied further in this study to explain the role of chemical additives on particle size and thus on deinking efficiency. Therefore, a series of trials was done with increasing levels of one or more of the chemicals studied.

The percentage of the examined area covered by ink particles larger than 10 µm is given together with relative (all per 1000) ink particle size distributions.

4. RESULTS AND DISCUSSION

4.1. Pulping chemistry

4.1.1. Alkalinity

The need for alkalinity in deinking to facilitate ink release by swelling the fibers and by saponification of the ink binders is well known (6-8) in the recycling of wood containing waste paper.

Total alkalinity is calculated as:

$$\% \text{ T.A.} = \% \text{ NaOH odp} + 0.112 \% \text{ silicate odp.}$$

We found that as much in the presence as in the absence of peroxide, the optimum total alkalinity is independent of the amount of silicate used (Fig. 1, 2).

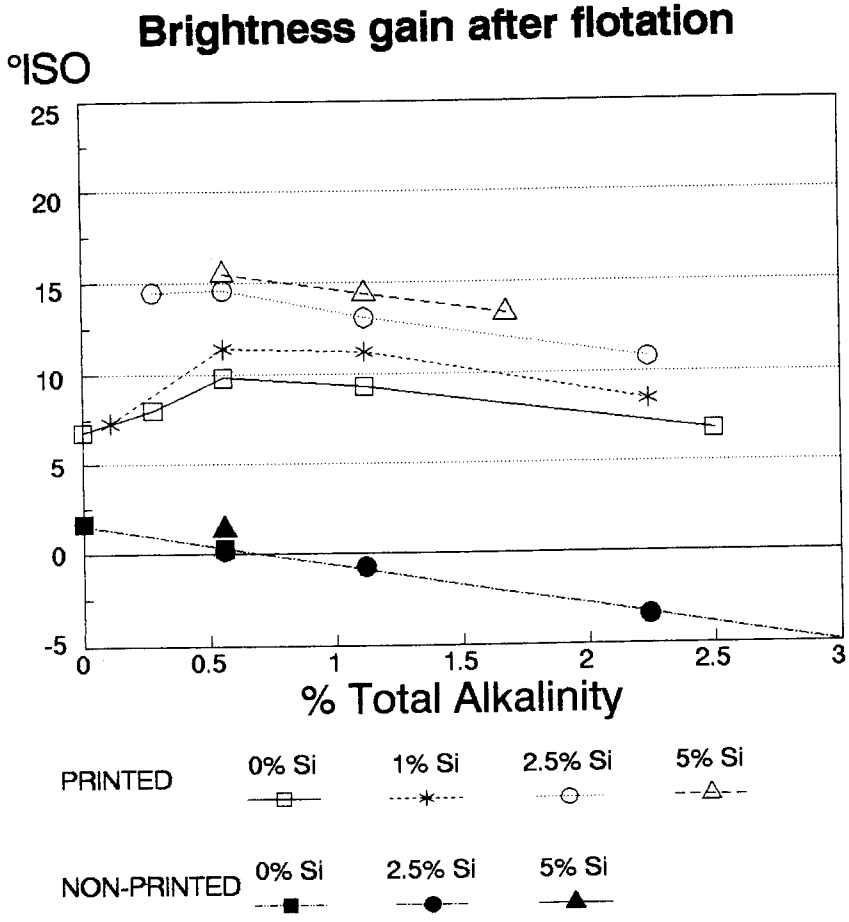

FIGURE 1: Brightness gain versus T.A., 0, 1, 2.5, 5% Silicate, 0% H_2O_2

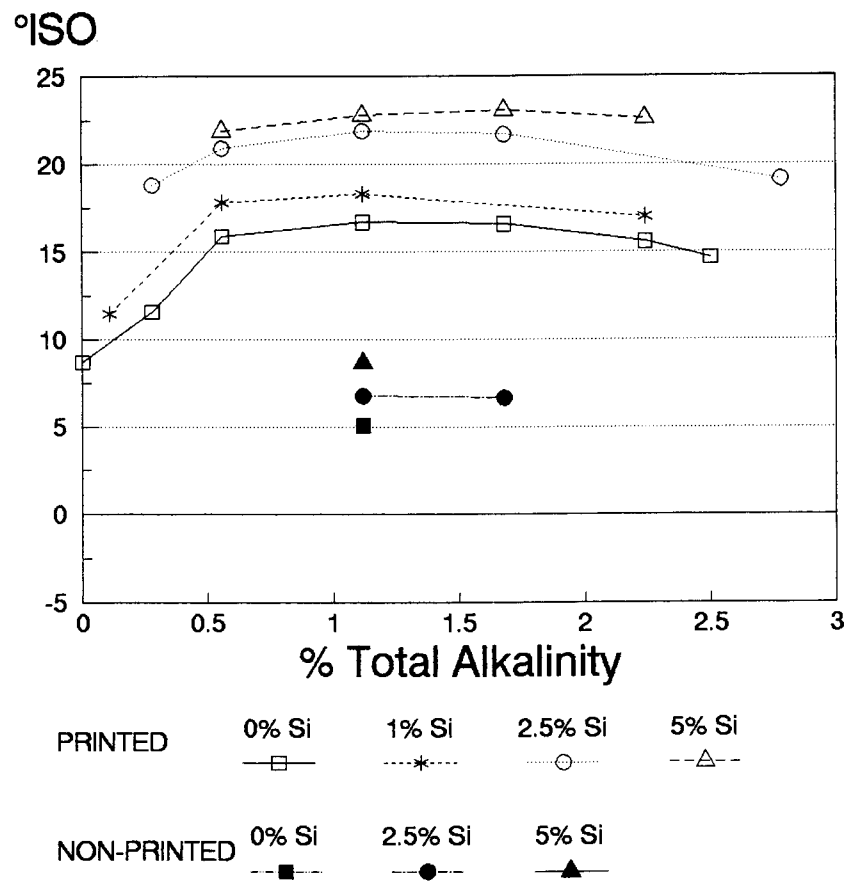

FIGURE 2: Brightness gain versus T.A., 0, 1, 2.5, 5% Silicate, 2% H2O2

In the absence of peroxide, a brightness gain of 3 °ISO was obtained by adding only caustic soda. By adding higher levels of alkalinity, a brightness drop was observed. The brightness drop is not related to deinking since the brightness curve versus total alkalinity obtained with non-printed furnish showed the same slope (Fig. 1). The observed alkaline darkening is due to the reversion of the bleached lignin to more coloured components.

4.1.2. Sodium silicate

Much research has been done on the role of sodium silicate, not only in deinking but also in mechanical pulp bleaching (9-11). The use of sodium silicate in pulp bleaching is associated with the stabilisation of hydrogen peroxide.

In the pulper, sodium silicate has an important role as an ink collector. The brightness gain, due to the application of silicate, is independent of the brightness gain due to the use of peroxide. This is shown by the parallelism between the two curves in figure 3. At low alkalinities such as found optimal for the pulper, the stabilisation of hydrogen peroxide by complexation of metal ions is not necessary.

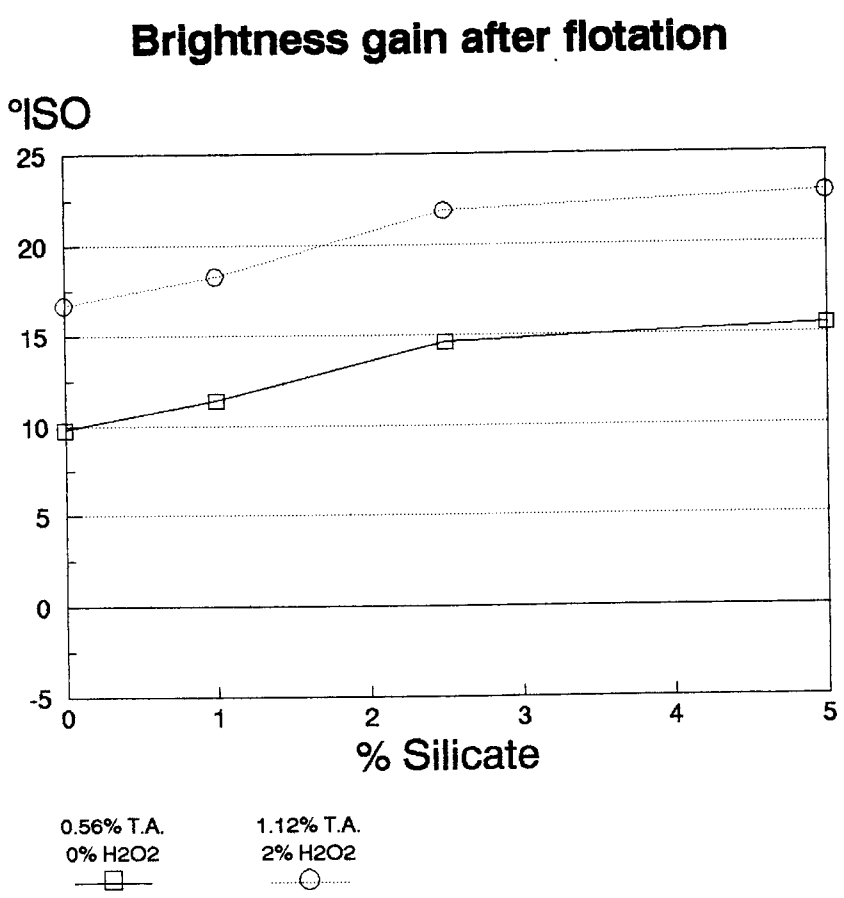

FIGURE 3: Brightness gain versus [Si], 0, 2% H2O2, optimum total alkalinity

Insoluble calcium and magnesium silicate complexes agglomerate ink particles smaller than 10 µm to form larger particles. This is shown by an increasing percentage of measured area covered by ink (Fig. 4) and, especialy in the larger size classes, an increasing number of ink particles (Fig. 5). The result is a more efficient ink removal by flotation and therefore a higher brightness after flotation.

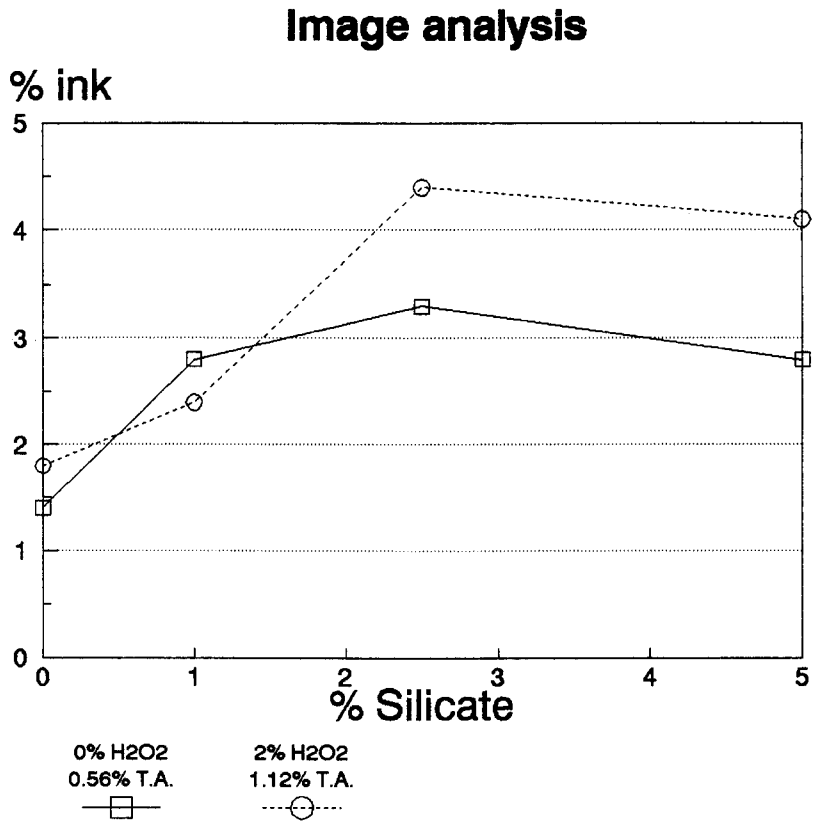

FIGURE 4: % of measured area covered by ink particles larger than 10 μm 0 - 2% H2O2

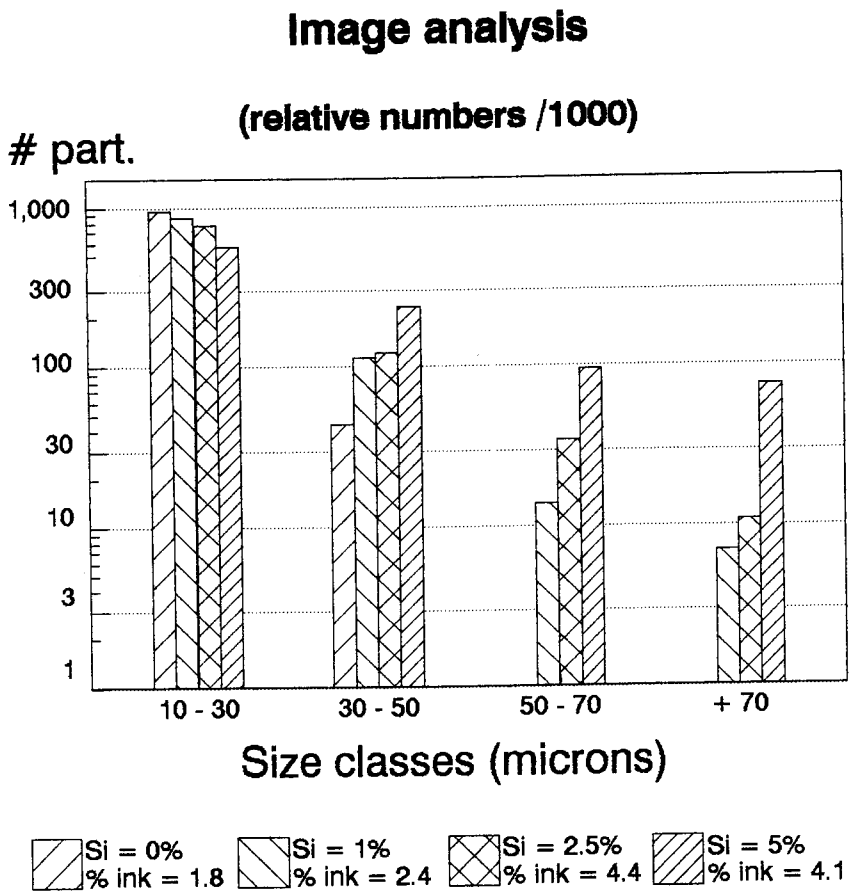

FIGURE 5: Number of ink particles per 1000 in each size class

2% H2O2, 1.12% T.A., 0 - 5% Si

4.1.3. Hydrogen Peroxide

First, the use of hydrogen peroxide in the pulper was studied. In a second part of the study, these results were compared with the use of all or a part of the total amount of hydrogen peroxide in a post-bleaching stage (see 4.3.).

The brightness gain obtained by using hydrogen peroxide in the pulper is a result of bleaching the support, i.e. the fibers. As shown by figure 6, the brightness gain due to the use of hydrogen peroxide is the same for printed and non-printed paper.

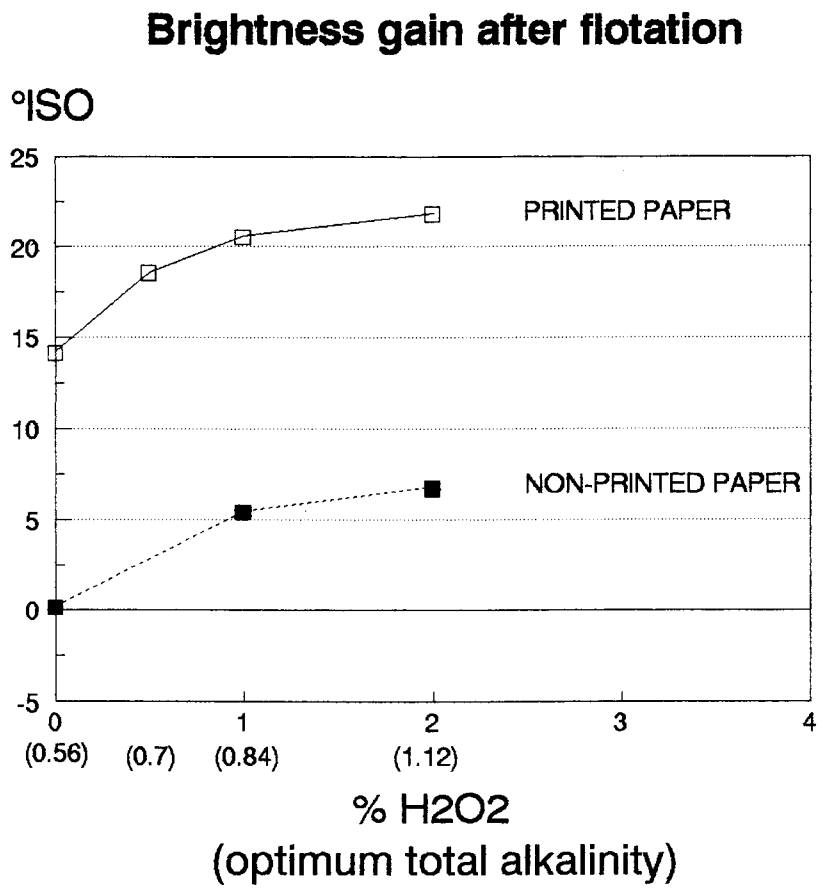

FIGURE 6: Brightness gain versus [H2O2], 2.5% Silicate, optimum total alkalinity

The optimum total alkalinity depends on the peroxide concentration used (Fig. 7). Without peroxide in the pulper, the brightness decreases rather quickly as soon as the optimum total alkalinity is exceeded.

With peroxide application in the pulper, the brightness curve shows a plateau versus the total alkalinity level. The brightness stability versus changing alkalinities was maintained as long as some residual peroxide remained after the pulping stage.

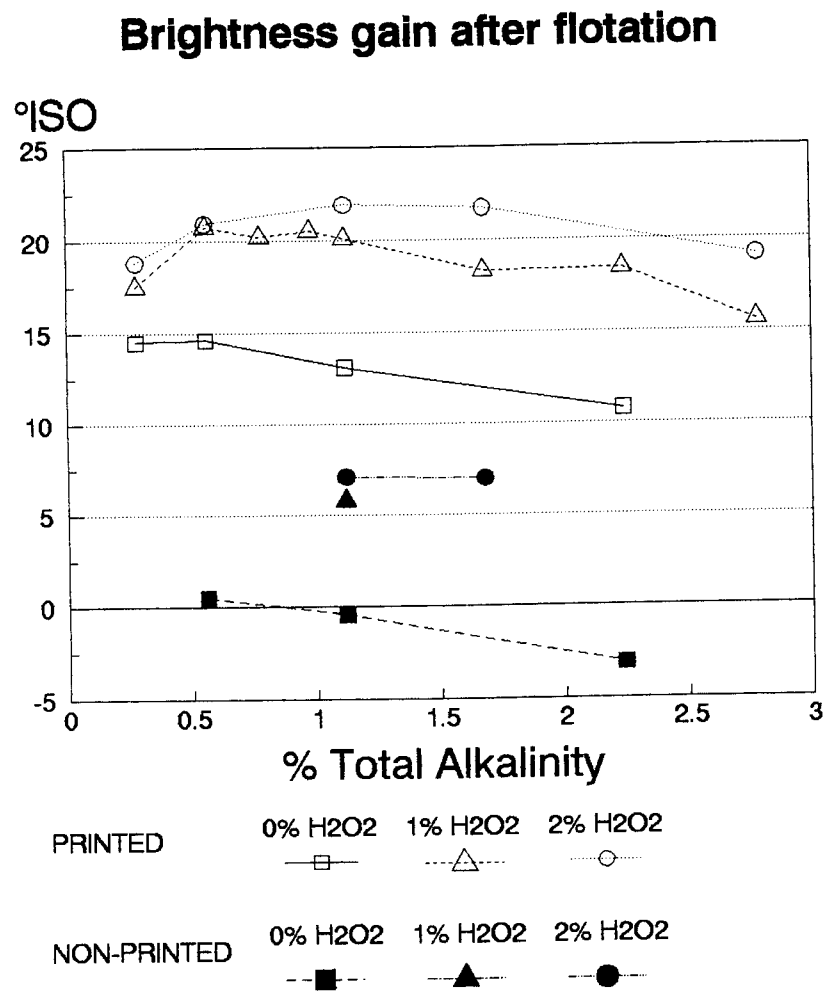

FIGURE 7: Brightness gain versus T.A.,
0, 1, 2% H2O2
2.5% Silicate

Another way to show the importance of peroxide utilisation in the pulper is demonstrated in figure 8. The higher the peroxide level, the higher the final pulping pH can be before the pulps starts to darken.

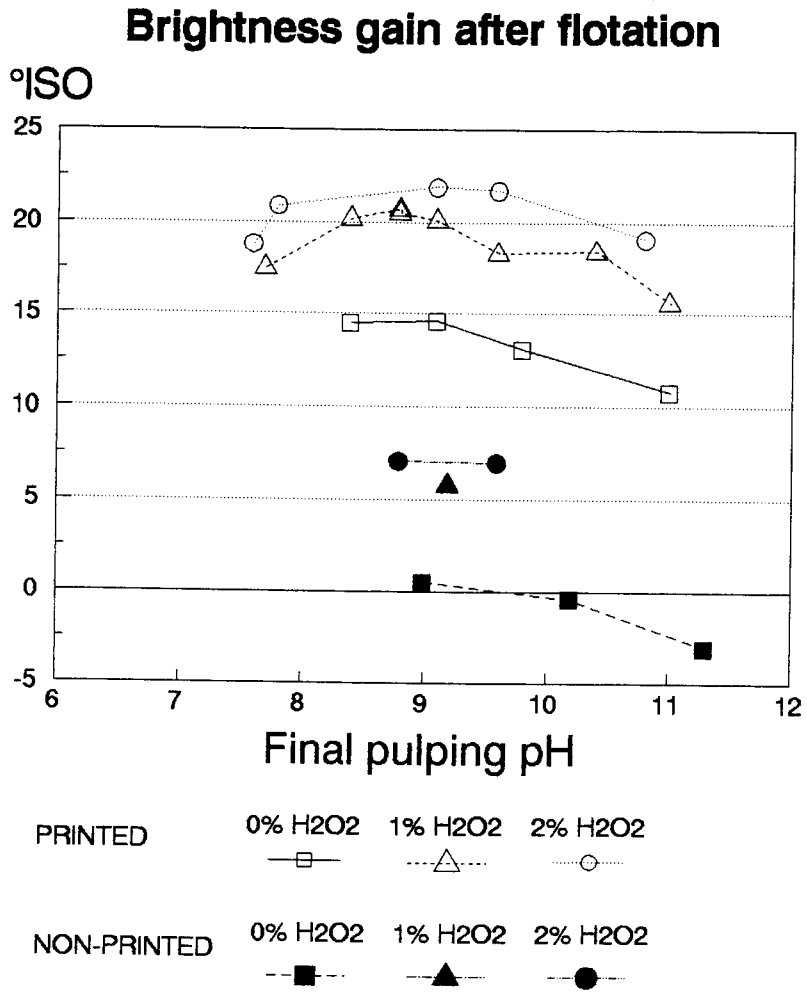

FIGURE 8: Brightness gain vs pulping pH
0, 1, 2% H2O2
2.5% Silicate

The pulping conditions (temperature, consistency and retention time) used in the first part of this study are certainly not optimal for bleaching. For the second phase (post bleaching) these conditions were improved.

4.2. Flotation

Before discussing post-bleaching, some flotation parameters will be discussed. The importance of pH control during the flotation and the influence of water hardness on flotation were studied.

4.2.1. Flotation pH

Three pulping stages were carried out with different addition levels of peroxide (0, 1, 2% odp). For all three, 2.5 % sodium silicate was used. The level of caustic soda was the optimum addition level earlier determined (0.3, 0.5, 0.8% odp). The flotation pH was changed with addition af caustic soda or sulfuric acid to the pulp, already at 0.8% consistency. As shown in figure 9, an initial flotation pH below 9 is needed to avoid alkaline darkening.

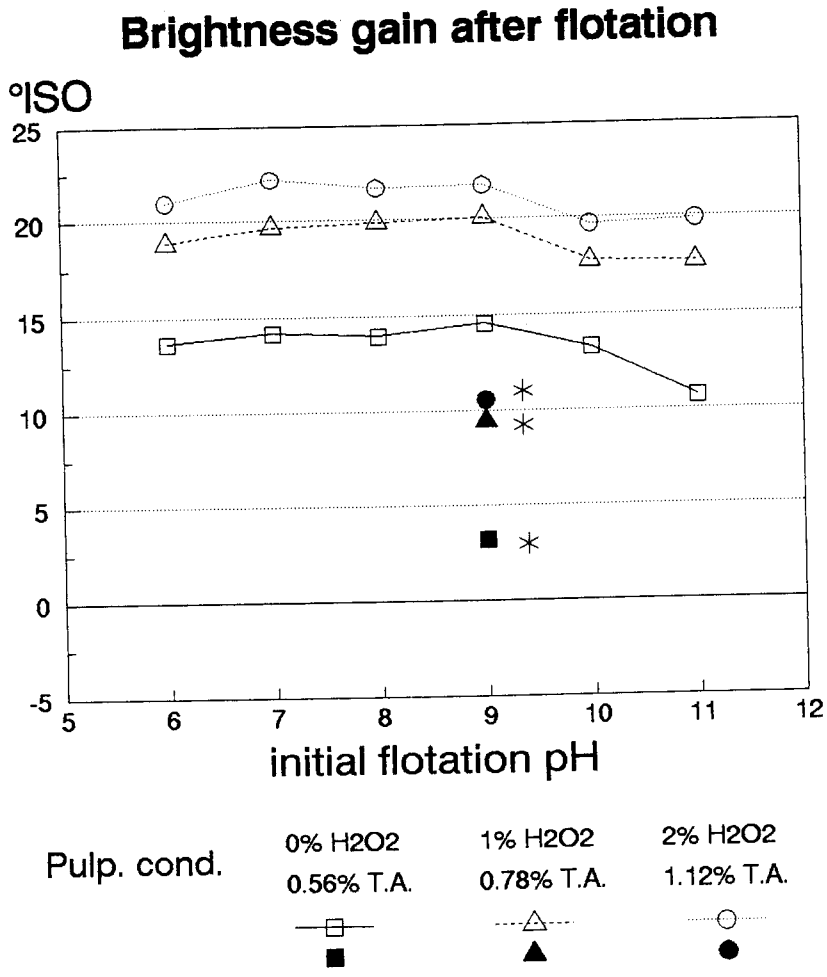

FIGURE 9: Brightness gain vs flot. pH
0, 1, 2% H2O2
2.5% Silicate

4.2.2. Water hardness

Water hardness is an indication of the concentration of Ca^{2+} and Mg^{2+} ions in solution. These ions are necessary in flotation to make the connection between the air bubbles and the ink particles. The influence of water hardness on brightness and on flotation yield and ash content was studied.

As shown by figure 10, a minimum of 5 to 10 °dH is necessary for good flotation. The brightness drops slightly with higher hardness. The yield and ash content are more influenced by the hardness of the process water. At too high water hardnesses, fines and especially fillers show a tendency to float with the ink particles.

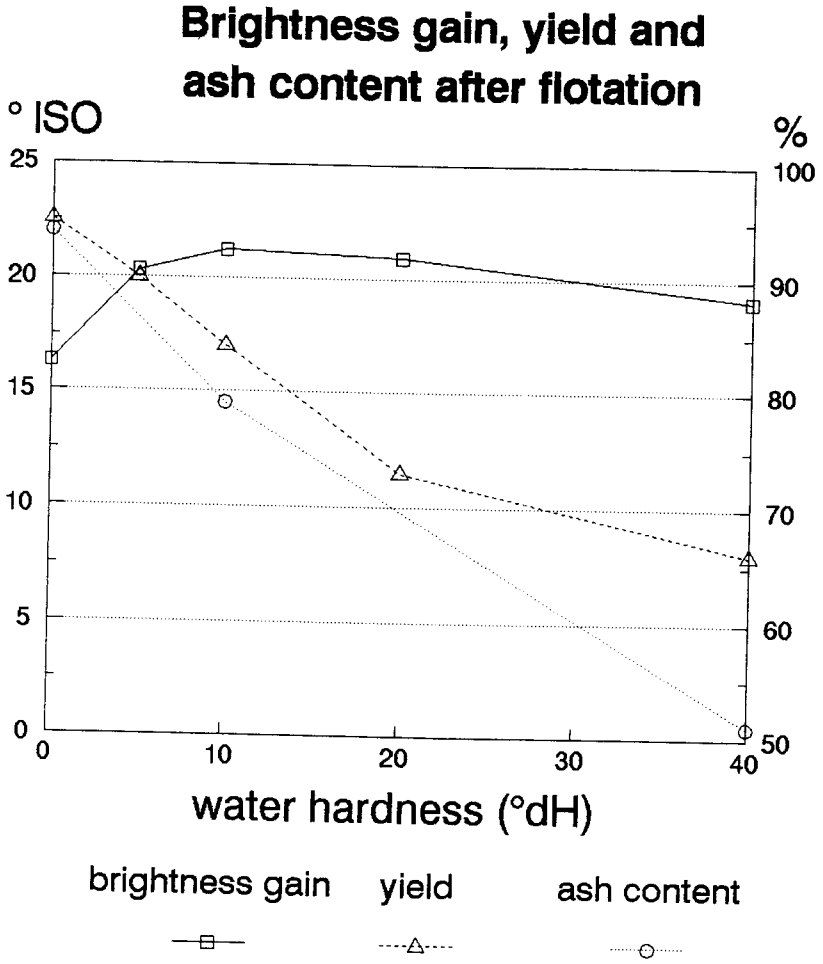

FIGURE 10: Influence of water hardness

4.3. Post bleaching

Post bleaching trials were performed in polyethylene bags in a warm water bath. The consistency, temperature and retention time were kept constant at respectively 25%, 70 °C and 60 minutes. The concentration of peroxide was varied between 0 and 4% odp. Caustic soda and sodium silicate levels were optimised for the different addition levels of peroxide. Figure 11 illustrates the optimisation of total alkalinity for different levels of hydrogen peroxide and for each, an earlier optimised sodium silicate level.

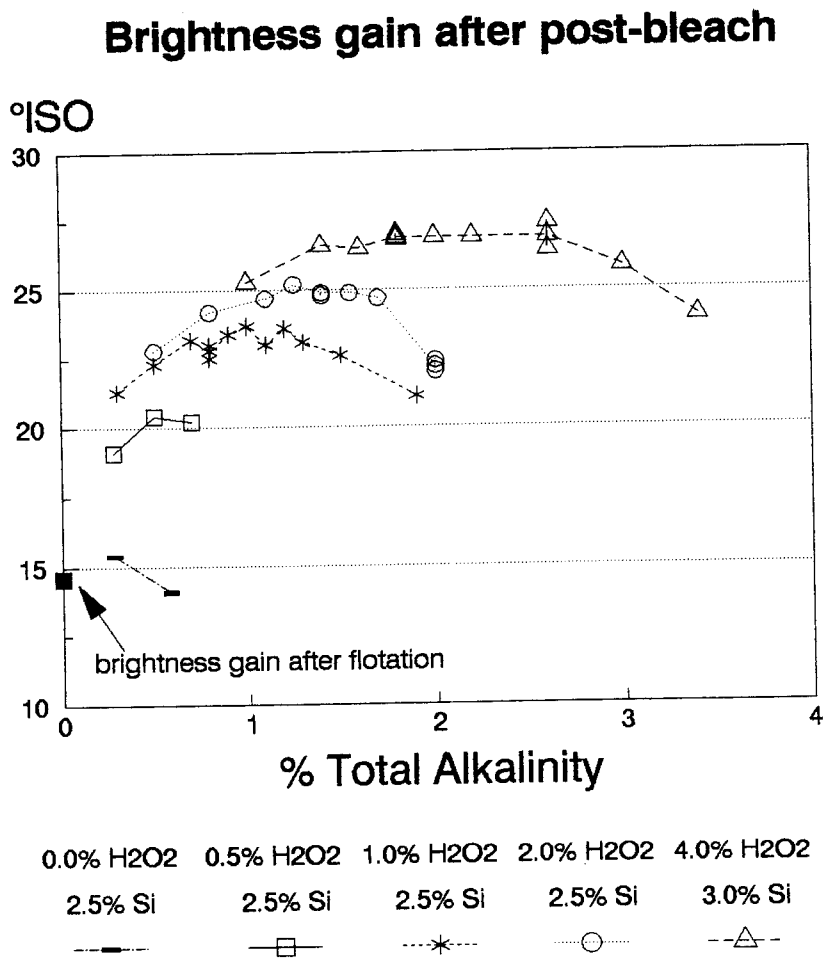

FIGURE 11: Brightness gain versus T.A., 0, 0.5, 1, 2, 4% H2O2 optimum silicate level

The brightness gains resulting from post bleaching were compared with these obtained by using peroxide in the pulper (Fig. 12). It is shown that the post bleaching conditions used are more efficient for hydrogen peroxide bleaching than those in the pulper.

The optimum total alkalinity levels are related to the experimental conditions. So, separate optimisation of caustic soda and sodium silicate is necessary for the pulper and the post bleaching stages.

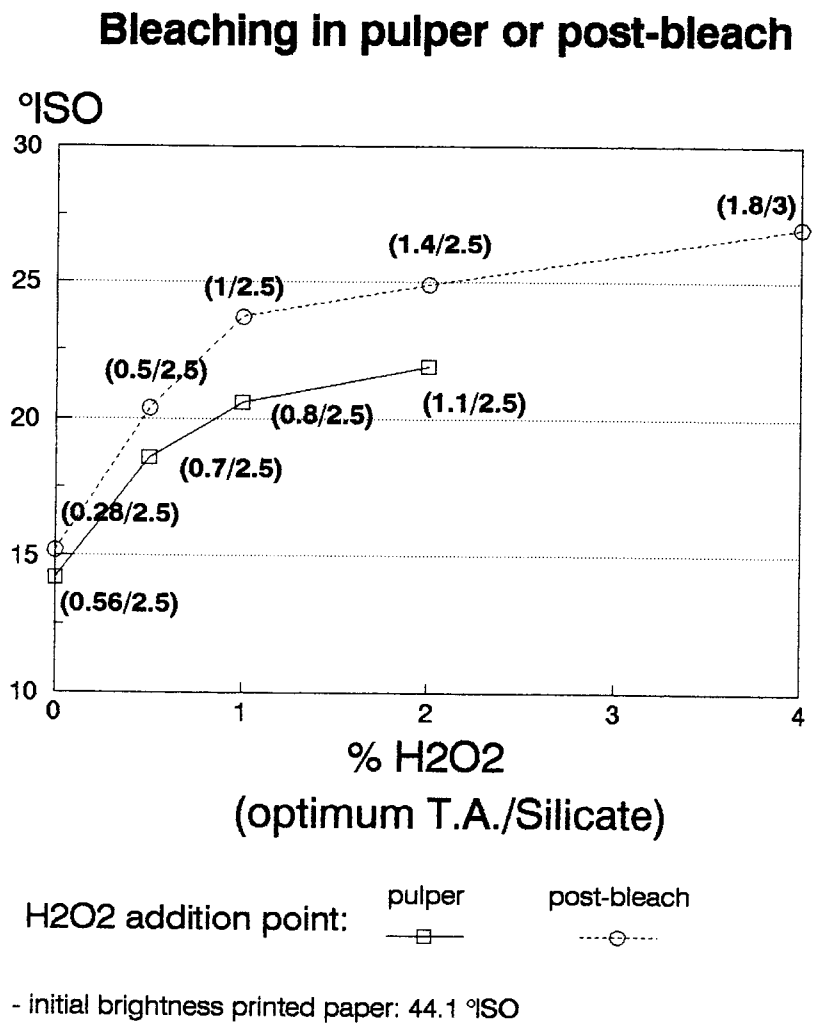

FIGURE 12: Brightness gain versus [H2O2], optimum Silicate optimum total alkalinity

Figure 13 shows the brightness gain versus the total level of peroxide applied. When only final brightness is considered, and when the levels of caustic soda and total alkalinity are well optimised, no advantage is found in using part of the total applied hydrogen peroxide in the pulper. Nevertheless, a small amount of peroxide in the pulper can be recommended to ensure brightness stability versus changing total alkalinity.

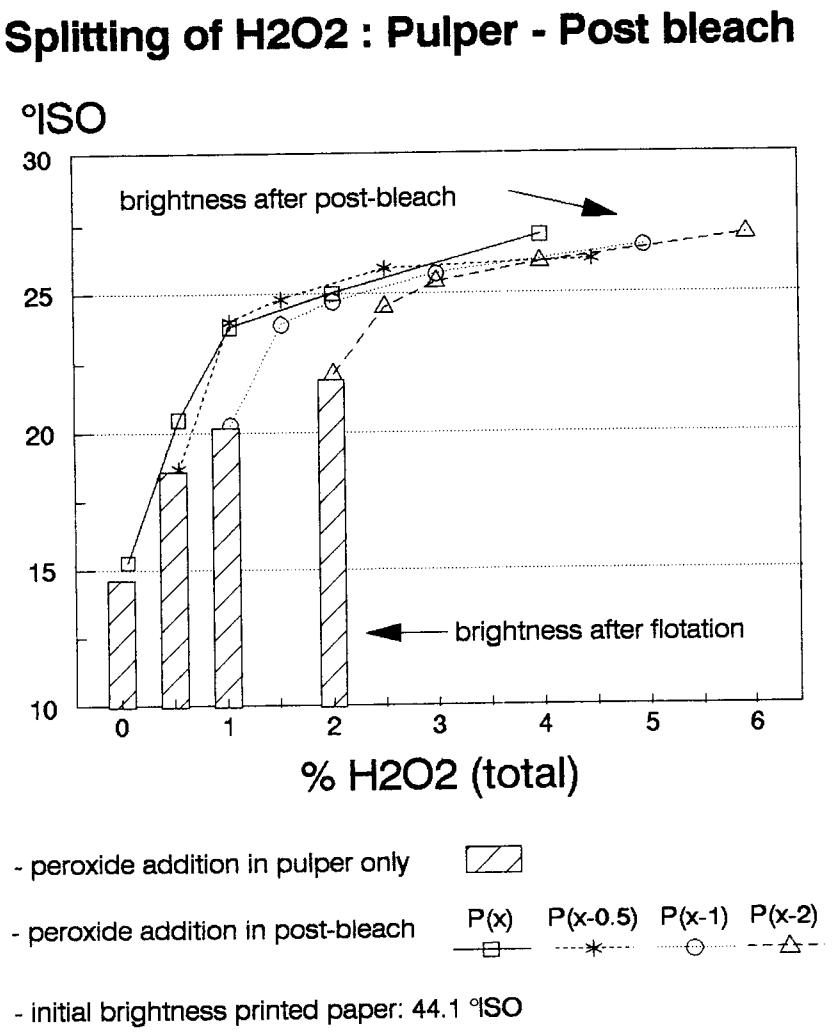

FIGURE 13: Brightness gain versus [H2O2], optimum Silicate optimum total alkalinity

5. CONCLUSIONS

The role of chemical additives related to the use of hydrogen peroxide was investigated. With the aid of image analysis, a difference could be drawn between brightness improvements due to deinking and bleaching and thus between pulping chemistry and bleaching chemistry.

In the pulper, alkalinity is necessary for swelling the fibers and thus for detaching the ink particles from the fibers. Too high total alkalinity levels cause alkaline darkening. This can be avoided by the use of hydrogen peroxide in the pulper. Even though the pulping conditions are in general not ideal for hydrogen peroxide bleaching, a small brightness gain is obtained due to bleaching.

Once the ink particles are detached from the fibers they have to be separated from the fibers by flotation. A minimum of 5 °dH water hardness is needed to be able to float ink particles. To increase the flotation efficiency particles, with the right size must be formed. This can be done by adding sodium silicate in the pulper. Insoluble calcium and magnesium silicate complexes agglomerate small ink particles and form ink particles of a suitable size for flotation.

Post-bleaching a deinked pulp which has not been treated with peroxide in the pulper, results in higher final brightness than using the same amount hydrogen peroxide directly in the pulper. Nevertheless, it can be recommended to use a small amount of peroxide in the pulper to ensure brightness stability versus changing total alkalinity levels.

6. ACKNOWLEDGEMENTS

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