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Deinking Difficulties Related to Waterbased Ink Printed Papers

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1. Introduction

Waterbased ink printed papers lead to deinking difficulties which can make conventional flotation deinking plants inefficient.

For some years, many people including inkmakers, chemical and machinery suppliers and research institutes have been working in order to improve the deinking efficiency of mixtures of wastepaper containing water-based printed papers and, in particular, flexoprinted newspapers.

The aim of this paper is to discuss the causes of deinking difficulties and to present the various approaches proposed to solve them : development of new inks which are deinkable in conventional processes, developments of chemicals able to collect waterbased inks in conventional deinking conditions and development of new processes efficient to deink mixtures of conventional and waterbased inks.

2. The deinking process

Deinking lines are made up of a combination of the various techniques described previously. The number of stages in the process depends on the grade of the furnish and the quality requirement of the deinked pulp to be produced.

2.1 Single-stage deinking

Fig. 1 presents a basic single-loop conventional deinking plant.

This flow sheet corresponds to the mills producing deinked pulp for newsprint or the back layer of multiply board from sorted wastepaper. That was the structure of most mills 10 years ago.

Wastepapers are defiberized in a medium consistency pulper (15 to 18% consistency).

After dilution, coarse screening removes large contaminants such as plastic films and wet-strength papers. High density cleaning removes heavy contaminants such as staples and sand.

Hole screening and slot screening are performed at medium consistency (up to 4%). Then the pulp is diluted down to between 1 and 1.4% consistency and submitted to flotation. Cleaning stages (heavy and lightweight) take place after flotation, generally after a complementary dilution (down to 0.7%). A fine slot screening stage can be implemented after cleaning. Then the pulp is thickened on a disk filter.

The white water is reused for dilution, in the various stages of the process. After the filter, the pulp is stored or diluted with water from the paper machine.

The process can be completed by hot dispersion and bleaching in order to improve pulp quality or by washing equipment to remove fillers and fines to produce pulp for

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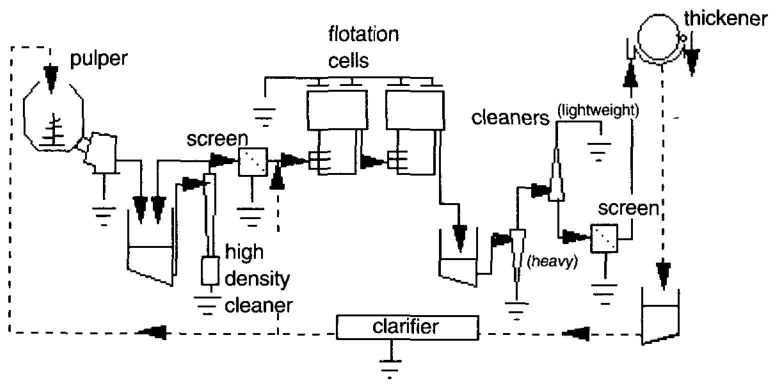

Fig. 1. Basic flow-sheet diagram of a flotation deinking plant (production of DIP for newsprint from sorted wastepaper).

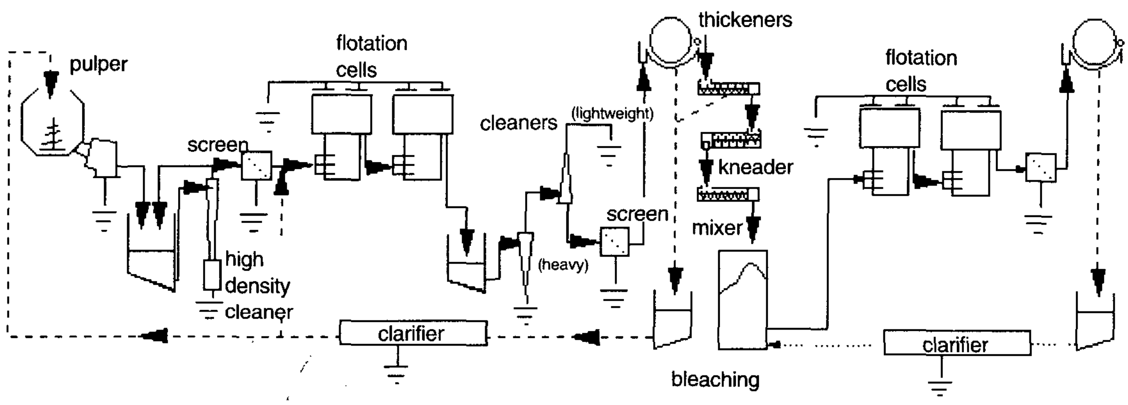

Fig. 2. Multistage deinking process.

tissue paper.

2.2 Multi-stage deinking

The production of higher quality pulp requires multi-stage deinking, an example is given Fig. 2.

3. Waterbased Print and Conventional Alkaline Deinking

3.1 Waterbased print

The furnish of deinking mills can contain various types of waterbased print, the most common is waterbased flexoprinted newspaper but some magazines and packaging materials can also be printed with waterbased ink.

Fig. 3 shows results of conventional laboratory deinking tests for newspapers printed by letterpress, offset and waterbased flexography.

Flotation of letterpress or recently printed offset newspapers leads to good deinking results, a well known decrease of brightness is observed with ageing of offset newspapers.

Flotation deinking of British and Italian

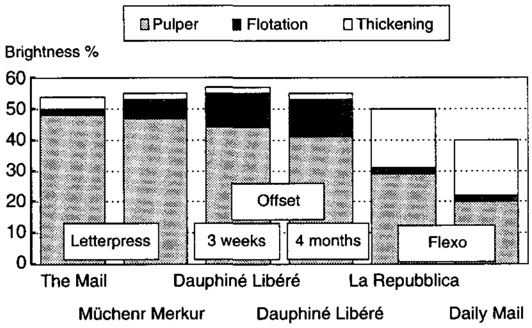

Fig. 3. Conventional laboratory deinking. Various newspapers.

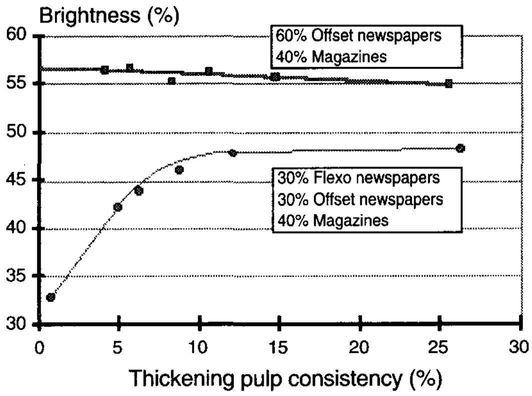

Fig. 4. Effect of thickening on deinked pulp from flexo and offset newspapers.

flexoprinted newspapers leads to a very low brightness pulp.

After flotation, the thickening of the deinked pulp has little effect in the case of letterpress and offset newspapers, but leads to an increase of about 20 % brightness with waterbased flexoprinted newspapers ; this increase is due to the removal with water of small flexo ink particles ; thickening waters are dark and in an industrial process this ink contained in the process water would be recycled and make the deinking process inefficient.

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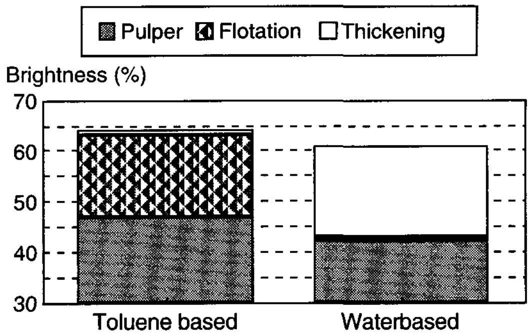

Fig. 5. Conventional laboratory deinking. Toluene based and waterbased rotogravure print.

Fig. 4 shows this difference of behaviour during thickening : with flexo, the final brightness depends mainly on the consistency of thickened pulp while little change is observed with offset.

Waterbased rotogravure print could also be an important concern for deinkers. We received the first sample of experimental waterbased rotogravure print in 1992. Fig. 5 shows the results obtained in the laboratory when deinking experimental waterbased printed magazines. The conventional alkaline deinking of waterbased printed magazines is as inefficient as is the conventional deinking of flexoprinted newspapers.

In 1995, we received samples of print made on industrial machines. These samples where deinked in the pilot plant and the results were as bad as in the previous tests ; no brightness gain during the flotation stage.[1] Similar results have been also obtained in Canada.[2]

Some waste from printing shops (white

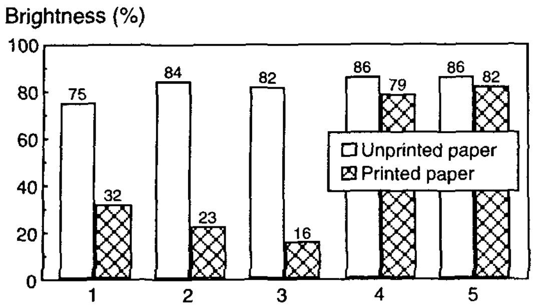

Fig. 6. Deinking results for some packaging papers.
1 : Pet food bag, flexo, waterbased varnish
2 : Pet food bag, flexo, waterbased varnish
3 : Cement bag, flexo
4 : Food packaging, rotogravure, cellulosic varnish
5 : Wine label, offset

paper) of packaging materials can be recycled in deinking plants.

Some samples of flexoprinted packaging papers have been deinked (laboratory scale) and compared to samples printed by other process. As well as newspapers and magazines, packaging wastes printed with waterbased ink lead to poor deinking results (Fig. 6).

A strong tendency to producing specks with samples printed by using the rotogravure process has been observed.

3.2 Causes of deinking difficulties

The causes of deinking difficulties are now well known; the small size of ink particles[3] and the lack of hydrophobic character of the ink[4] are the main reasons.

3.2.1 Ink composition

Waterbased flexographic inks are based on acidic resins (mainly acrylic resins) which become water soluble or dispersible when neutralised with organic bases such as amines. After printing, they become bleed resistant as the amines are dissipated by volatilisation or absorption by newsprint. In conventional deinking conditions i.e. in alkaline conditions, ink binders are solubilized and very small particles of ink are dispersed into the pulp suspension. Their removal from fibres is facilitated.[5]

Thus it can be stated that these water-dispersed ink particles are difficult to remove by flotation.

The various components which can be used in flexographic inks have been reviewed by Chabot et al.[6] The main difference between flexographic ink and other ink is found in the carrier and binders. Pigments are identical, but their size is different, in flexo ink the size is smaller so that the pigment will stay dispersed in the water phase. Various resins in solutions, colloidal dispersion or emulsion and various amines (including ammonia and triethylamine) can be used in flexo ink compositions.

Some differences in deinkability of flexoprinted papers can be related to the differences in the resins and amines used to manufacture the flexo inks.

Deinking trials performed under the same deinking conditions, with two issues of the same Italian newspaper, but printed with inks from various suppliers have shown very different brightness : 26 and 32% after the pulping stage, 30 and 44% after flotation.[7]

The differences of behaviour between European and North American flexo newspapers are often reported in conference discussions but no accurate comparisons have yet been published. The water solubility of resins in alkaline conditions is different. US resins have lower solubility and print has lower quality, whereas European resins have higher solubility and print has better quality.

3.2.2 Redeposition of ink on fibres

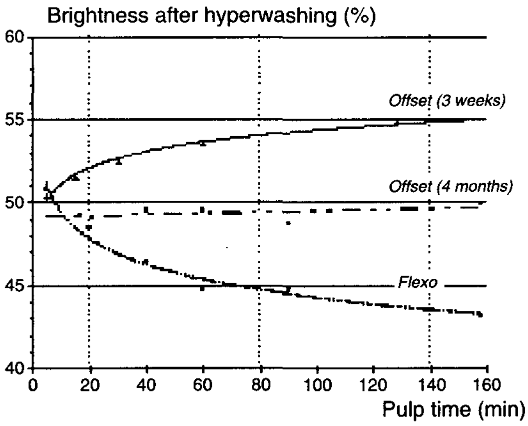

Fig. 7. Redeposition phenomena. Comparison of an increase of pulping time (laboratory medium consistency helico pulper (9 % consistency). Conventional deinking conditions. Pulping times have been exaggerated in order to emphasize phenomena.

Another problem in deinking of flexographic printed newspapers is the tendency of the ink to redeposit on fibres.

The importance of this phenomena depends on various parameters of the deinking process, it increases with pulping time (Fig. 5) and with pulping consistency.

The control of hyperwashed pulp brightness is a way to control the detrimental effect of ink redeposition.

In Fig. 7, it can be seen that the same increase of pulping time in the case of offset printed newspapers induces the opposite effect: the improvement in ink detachment induces an increase of the brightness of hyperwashed pulp. This effect is more important for recently printed than for old newspapers.

According to Mah[8] the tendency of ink particles to re-attach to fibres includes the concept that some ink particles would enter in the fibre lumens through the fibre ends.

Some bad results obtained by washing deinking[9] can also be related to an introduction of fine ink particles in fibre opening or adsorption on the fibre surface when pulping at high consistency (18%), The brightness of the washed pulp can be increased from 40 % to 50 % if pulping is performed at low consistency (4%).

Chabot et al.[10] have shown that the conditions (acidic pH or presence of sodium oleate and calcium ions) which increase the agglomeration of flexo ink and their floatability in the absence of fibres (see § 4.1.2) increase the retention of ink in the pulp mat. Redeposition does not occur during flotation, but ink particles get trapped by filtration during sheet formation.

Ben et al.[11] have demonstrated that the small ink aggregates (0.5-3 μm) adsorbed, in the presence of calcium ions and calcium soaps, on the fibre surface during a pulp thickening stage, cannot be dislodged from the fibre mat by the application of calcium-neutralising chemicals in the displacement fluid or by an increase of hydrodynamic forces via a higher flow rate.

3.2.3 Difficulties in water clarification

Another concern when deinking water-based-ink-printed papers is related to difficulties in water clarification, especially if washing is chosen as the technique for the ink removal.

In 1989 Putz et al.[3] indicated that even with the good washing results of water-based flexo ink, the deinking problems are not solved, but are only transferred to clarification of the wash water which is still dark after treatment.

Fernandez and Hodgson[12] have related the difficulties in flocculation of flexo ink particles to the adsorption of the acrylic resin binder onto carbon black which contributes significantly to an electrostatic barrier against flocculation (particularly at pH of approx. 8).

4. Progress in Deinking Water-based Print

4.1 Adaptation of the conventional deinking process

4.1.1 Pulping conditions

Some changes in pulping conditions can improve deinking of flexographic printed newspapers and increase the brightness of deinked pulp.

On a laboratory scale, a reduction of pulping time (which is possible from 15 min to 5 min with 100% newsprint) can increase the brightness of the floated pulp from 32 up to 37%, this effect is certainly due to a reduction of ink fragmentation but, unfortunately it is not possible to transfer such a reduction in pulping time to industrial mixed supplies.

4.1.2 Water hardness. Calcium soap physical chemistry

High water hardness (Fig. 8) increases the brightness after flotation but reduces it after

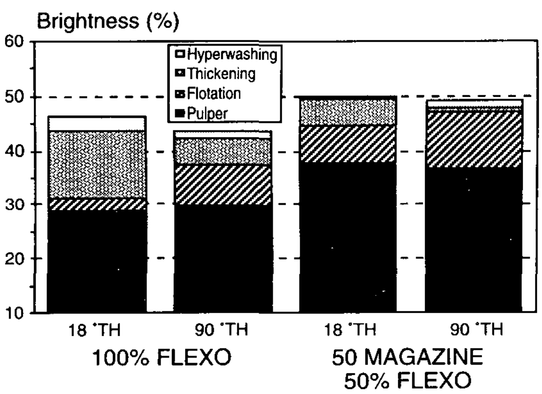

Fig. 8. Effect of water hardness on deinking of flexographic newspapers. Low consistency pulping without hydrogen peroxide.

thickening or hyperwashing. This is probably due to a diminution of ink dispersion which improves flotation efficiency and an increased redeposition of ink onto the fibres which reduces final brightness. Results describing a decrease of brightness in flotation + washing deinking when increasing water hardness have also been published in North America.[13, 14]

Much more fundamental work has been performed in Canada regarding the interaction between calcium soap and flexo ink particles.

McLennan and Pelton[15] have studied the conditions in which very small flexo ink particles (dispersed (without fibres) "react" with pre-made calcium soap particles. One of the main observation was that when the calcium concentration is greater than 1.0 mM, flexo ink spontaneously deposits on calcium soap particles.

Dorris and Nguyen[16] have reported results of trials performed with flexo ink dispersion without fibres. These trials have shown that flexo ink can be floated in alkaline conditions by using conventional soaps provided that the dissolved calcium concentration exceeded 100 mg/l. The causes of poor results obtained in mills using similar chemistry are considered to be due to interference with fibres and paper constituents and particularly ink redeposition on fibres.

When using a deinking chemistry with calcium soap, the adverse role of fibres on flotation of flexo ink particles has been later pointed out with a model system.[17] The flotation efficiency decreased markedly as fibre consistency increased, some mechanical parameters (impeller speed, air flow rate) could improve flotation efficiency. Fibres acted negatively through a reduction of the equilibrium size of flexo ink aggregates.

Increasing water hardness can be considered as favourable for flotation efficiency but, on the other hand in washing deinking it can be considered that lower the water harness lower the washing efficiency. This consideration is consistent with the results of Fig. 8 describing a reduction of brightness during the thickening stage but also with Canadian works.[2, 11]

4.1.3 Prevention of ink redeposition

A reduction in ink redeposition by using appropriate chemicals such as CMC has been confirmed in our trials but no improvement of ink removal during the flotation process has been obtained.

* It has been shown[18] that appropriate chemicals such as CMC can reduce this redeposition.

* CTP trials (Fig. 9) did not show any improvement of ink removal during the flotation process. The brightness of the floated pulp remains too low while the brightness gain during thickening is increased. The brightness of hyperwashed pulp is also increased confirming the reduction of ink redeposition.

Some reductions in ink redeposition can also be achieved by using particular surfactants. Displectors (chemicals developed for washing-flotation processes which are both "dispersants" and "collectors" have been also evaluated during CTP trials as reducing ink redeposition.[19]

Various additives have been tested by Borchardt et al.[13] as antiredeposition agents, among them sodium polyacrylate, which is a common binder of flexographic inks, has been found to be an effective additive for reducing redeposition .

4.1.4 Development of chemicals adapted to removal of waterbased ink

One direction to improve deinking of flexo printed newspapers consists in developing properly adapted chemicals in order to improve flotation removal efficiency. Various papers about such work have been published since 1989.[13, 20-29]

Unfortunately, probably for commercial reasons, a lot of these papers do not give any information about the chemical nature of the additives which are claimed to improve deinking of flexo ink in conventional alkaline deinking conditions.

In the CTP we have tested many products on a laboratory scale. Only a few have given interesting results. The best of them were tested in a continuous process in the CTP

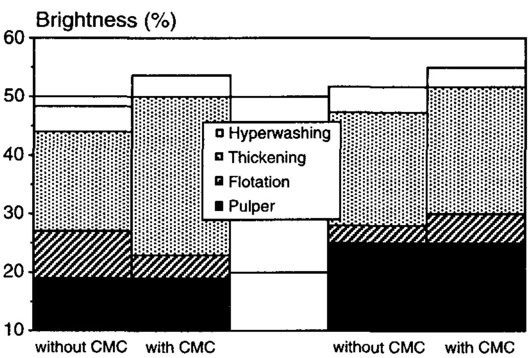

Fig. 9. **Effect of CMC on removal and redeposition of ink. Conventional deinking conditions.**

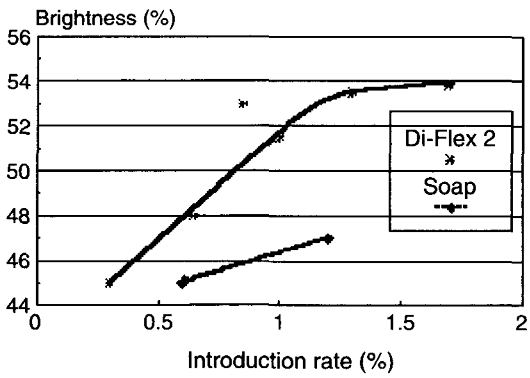

Fig. 10. Comparison of deinking aids on the CTP Pilot Plant. Mixtures with 30% flexo newspaper, 30% offset newspaper and 40% magazines.

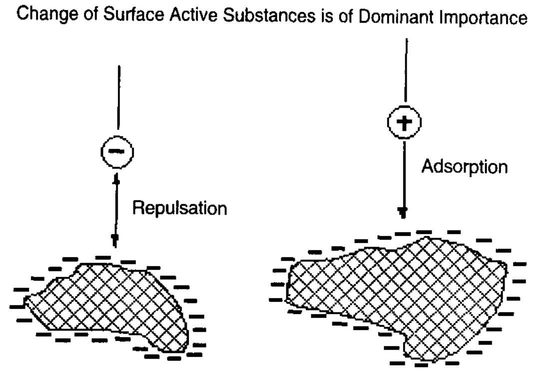

Fig. 11. Adsorption of surface active substances on hydrophilic particles (Putz et al.). [30]

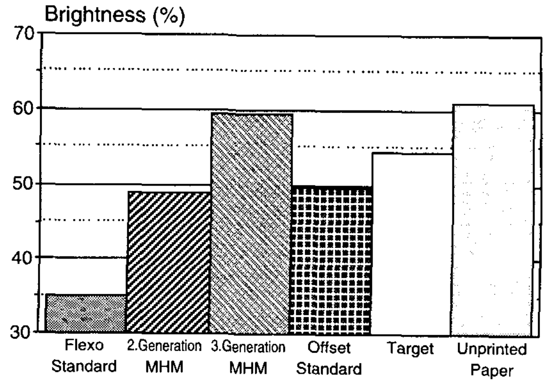

Fig. 12. Deinking results with standard and new flexo inks (Buchweitz).[31]

pilot plant (with reuse of the thickening water for dilution). The results, shown in Fig. 10 are rather interesting, although the amount of product required is rather high. The drawback is an increase of fibre loss (+ 3/5%).

According to the deinking model proposed by Putz et al.,[30] the surface charge of the particles is negative, and their character is hydrophilic ; the affinity between the particles and air bubbles is low. The authors suggest using cationic surfactants which can be adsorbed very well because they carry the opposite charge (anionic surfactants are repelled).

When disintegrating flexo wastepaper in deionized water with cationic surfactant a significant brightness gain can be obtained by flotation, the brightness gain was much higher than those obtained with anionic or non-ionic surfactants (Fig. 11).

4.2 Waterbased ink deinkable in conventional processes

Work to develop inks which can be removed in conventional processes has been carried out both in Europe and North America.

* The German ink manufacturer Michael Huber Munchen Gmbh claimed that water based inks which are deinkable in present flotation systems have been manufactured and that the latest developed inks have a deinkability comparable to standard offset newspapers (Fig. 12).[31] This company has applied for patent in which the ink composition includes cationic resins instead of polyacrylic acid.[32]

* In north America, trials performed in cooperation between a paper mill, a chemical supplier and inkmakers have led to a specially formulated flexo ink which has shown good deinking results on a laboratory stage. During an industrial trial with 25% of newspapers printed with this specially formulated ink, the brightness of the deinked pulp dropped 6 points and fine ink particles were observed in the deinking plant water system. If a pulp sample was subjected to further flotation deinking on a laboratory scale the pulp brightness recovered from 54 to 60%, which confirms that this ink is removable by flotation but a much longer residence time was required.[8]

4.3 Adaptation of process

Various processes for deinking mixtures

Table 1. Some processes proposed for deinking mixtures containing waterbased ink printed papers

Combination flotation and washing	Flotation + washing + increased peroxide introduction rate	(Clewley et al.)[33]
	Flotation + 3 washing stages	(Rangamannar et al.)[34]
	Washing + flotation (with secondary flotation of wash filtrate mixed with foam flotation)	(Matzke)[35]
Two flotation conditions	Alkaline flotation + acidic flotation	(Suss et al.)[36]
	Non alkaline flotation + alkaline flotation	(Galland and Vernac)[37]

containing waterbased ink printed papers have been proposed for the last 10 years, the main ones are summarised in Table 1 and described below.

4.3.1 Comparison of the various processes

Some of the processes described above have been compared in the CTP recycling pilot plant whth mixtures containing 30% of Italian or British flexoprinted newspapers. All the trials were performed in close water system .[38, 39]

All the processes tested with alkaline pulping conditions have led to low final brightnesses (maximum final brightness 55 %).

Best results are obtained with non alkaline pulping, flotation, peroxide bleaching in the kneader and alkaline flotation (final brightness 61 %). These results are related to :

1 / Less ink fragmentation in the pulping stage in non alkaline conditions. In the case of alkaline pulping, the ERIC value of the pulp after reslushing is higher than 2000, and is reduced to 1590 in the case of neutral pulping. This demonstrates a lower ink fragmentation which leads to a higher flotation removal efficiency in the first flotation stage and a higher final brightness at the process outlet.

2 / Less ink redeposition. Redeposition of flexo ink during high-consistency pulping has been pointed out in section 3.2.2, particularly when pulping at high consistency (18%).

Table 2. Characterisation of ink redeposition for neutral and alkaline pulping

Hyperwashed final pulp (outlet of the process)		
Pulping	ERIC value	Brightness
Neutral	< 100	61 to 64
Alkaline	200 to 300	54 to 57

Measurements on the hyperwashed final pulp give some interesting information (Table 2) :

For all the trials performed, the ERIC value of hyperwashed pulp resulting from non alkaline + alkaline deinking is lower than for pulp obtained with alkaline pulping and the brightnesses is higher demonstrating that a higher ink amount remains on the fibre, probably due to ink redeposition.

5. Conclusions

The cause of difficulties of removing the waterbased ink by flotation in a conventional deinking process are now well known : they are related to the small size of ink resulting from alkaline pulping and to their hydrophilic character. In some cases redeposition phenomena can also reduce their ability to be removed by washing.

Improvement of deinking of mixtures containing waterbased inks can result from various approaches :

* development of new chemicals which

can agglomerate the fine ink particles and enhance their removal by flotation. Some chemical suppliers claim to have developed such chemicals.

* development of new inks deinkable in a conventional alkaline process. Some ink suppliers claim to be able to produce such inks.

* development of new processes. This approach includes combinations of washing and flotation, with the consequent need for improvement of water treatment, and two-flotation stages, each stage being performed in different pH condition.

Development of inks which can be deinked in conventional conditions would certainly be the best solution for papermakers but some opinions consider that such ink would not lead to good print quality.

Concerning the newly developed flotation aids, opinions about their efficiency also disagree.

Our opinion is that for deinking plants using a low percentage of waterbased printed paper, chemical solutions will certainly be sufficient ; but if there is a strong development in the use of waterbased ink, the fundamental difference in properties between flexo and offset inks and the requirement of high brightness pulp will probably call for the use of a two-stage process.

In any case, the development of water-based inks which are claimed as more environ-mentally friendly due to the absence of solvent in the ink will lead to recycling difficulties : decrease of recycled pulp quality and/or increase of recycling costs : more expensive flotation aids, higher chemical demand for water treatment and higher investment costs.

Nowadays, waterbased inks are not "recycling friendly."

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