DIFFERENCES IN THE RECYCLING BEHAVIOUR OF PAPER PRINTED BY VARIOUS TECHNIQUES

NELA DUMEA, ZOLTAN LADO* and EMANUEL POPPEL**

SC Letea SA Bacău, Letea 17, Bacău 600122, Romania
**Ceprohart Brăila – Suceava Branch, Suceava 720019, Romania*
***"Gh. Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, Iaşi 700050, Romania*

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The diversification of existing printing methods represents a great challenge for papermakers who utilize wastepaper in production processes. Prior to reuse, secondary fibres are subjected to some processing steps, for recovering their initial papermaking potential. Depending on the extent of recovering, the obtained fibrous material will be more or less recommended for the production of new paper products.
The present paper approaches the deinking ability of offset, flexographic and digital prints in laboratory flotation deinking.

Keywords: wastepaper, deinked pulp (DIP), brightness, ERIC number, spots

INTRODUCTION

Recovered paper recycling is usually performed in specific complex processing equipments, according to the final utilization of the stock. Processing may include several steps, such as repulping in the presence of chemicals, screening, deinking by flotation or washing, final cleaning, thickening, hot dispersing and bleaching. Among the numerous factors determining the quality of the final deinked pulp (DIP), the most significant ones are the following: the method used in paper printing, ink composition, print age, storage condition and type of recycling.

Ink formulation is an essential factor in deinking. Common ink formulations, the ratio and role of each component are presented in Table 1.

As known, in the composition of ink, the solvent records significant percentages, its nature playing an important role in recycled paper deinking. The growing amounts of office paper printed mainly by xerographic and ink jet techniques with toner and water-based inks create additional removal problems in flotation recycling systems.

Obviously, the mills processing recovered paper choose the methods used in the printing stage as a function of the large variety of raw materials they have to process. Consequently, the selection of the optimal recycling methodology for each type of print is essential.

EXPERIMENTAL

The basic characteristics of the analyzed wastepaper are presented in Table 2.

Recovered paper samples were repulped and deinked under laboratory conditions similar to those of a single-loop industrial flotation plant. The deinked pulp was obtained in the following operation steps:

a. slushing under alkaline conditions:
- offset prints (40% newspaper/60% magazine),
- flexographic prints (100% newspaper),
- digital prints (high-grade graphic paper, HP laser printed with a mixture of cyan/magenta ink in a continuous central 2 cm wide strip print and an additional "a" letter print on the rest of the page);

b. slushing under neutral conditions of a flexographic print (similar to that of point a).

The chemicals used during alkaline repulping were similar to those indicated by the INGEDE[3]

(International Association of the Deinking Industry), known as a leader in promoting the recycling and reuse of recovered graphic paper.

The chemical dosage applied in alkaline deinking for recovering the original properties, as compared to the INGEDE Method 11, is presented in Table 3.

In neutral repulping of flexographically printed paper, a 0.1% dosage of non-ionic surfactant, produced by Eka Chemicals - Berocell 209, was used.

Methods and lab facilities

The working conditions applied and the laboratory facilities used are presented in Figure 1.

Table 1
Chemical composition, ratio and role of components in printing ink[1,2]

Component	Role	Description
Pigment (5-30%) Black: smut Cyan: phthalocyanines Magenta: azopigments and salts Yellow: azopigments	Absorb light to specific colour	Insoluble particles dispersed in a continuous phase (vehicle) represented by a transport phase and a binder
Binder (15-60%) Siccative oil (offset sheet) Natural resins (ink for newsprint) Phenolic resins (all kind of inks) Alkydals (offset inks) Acrylates (UV inks and water-based) Nitrocellulose (flexographic)	Link pigment particles to paper surface and contribute to gloss	Amorphous polymer materials as resins or vegetable oxidative oils
Solvent or portable phase (20-70%) Mineral oils (offset) Vegetable oils (offset) Toluene, xylol (rotogravure) Water (flexographic) Alcohols, esters, ketones (flexographic)	Contribute to ink fluidity	Solvent (boiling point < 100 °C) and/or oil (boiling point > 100 °C)
Additives (1-10%) Siccatives Non siccatives Wetting agents, biocide	Conduct to particular characteristics or improve certain properties	Chemicals with particular chemical formulation to fulfil a specific role

Table 2
Characteristics of the recovered paper samples under analysis

Characteristics	Unit	Newsprint		Magazine	Office paper
Printing method/base paper	-	flexo/uncoated	offset/uncoated	offset/coated	laser/high loaded
Print age	months	3	4	5	1
Basis mass	g/m^2	45	40	52	104
Apparent density	g/cm^3	0.75	0.57	1.04	0.87
Breaking length, long direction	m	4,890	5,333	5,256	3,270
Brightness	%	30.6(N)/24.5(A)	44.5	59.7	77.13
• slushed whole print	%	56.4	52.2	72.3	91.2
• unprinted edge	%	19.5	0.60	29.0	8.74
Ash					

N – non-ionic repulped; A – alkaline repulped

Table 3
Chemicals utilized in the alkaline method[4]

Pos.	Chemical	Dosage of chemical	
		Ingede 11	Our method
1	Sodium hydroxide	0.6%	0.7%
2	Sodium silicate	1.8%	1.5%
3	Hydrogen peroxide	0.7%	0.7%
4	Surfactant	0.8% oleic acid	0.7% Serfax MT 90

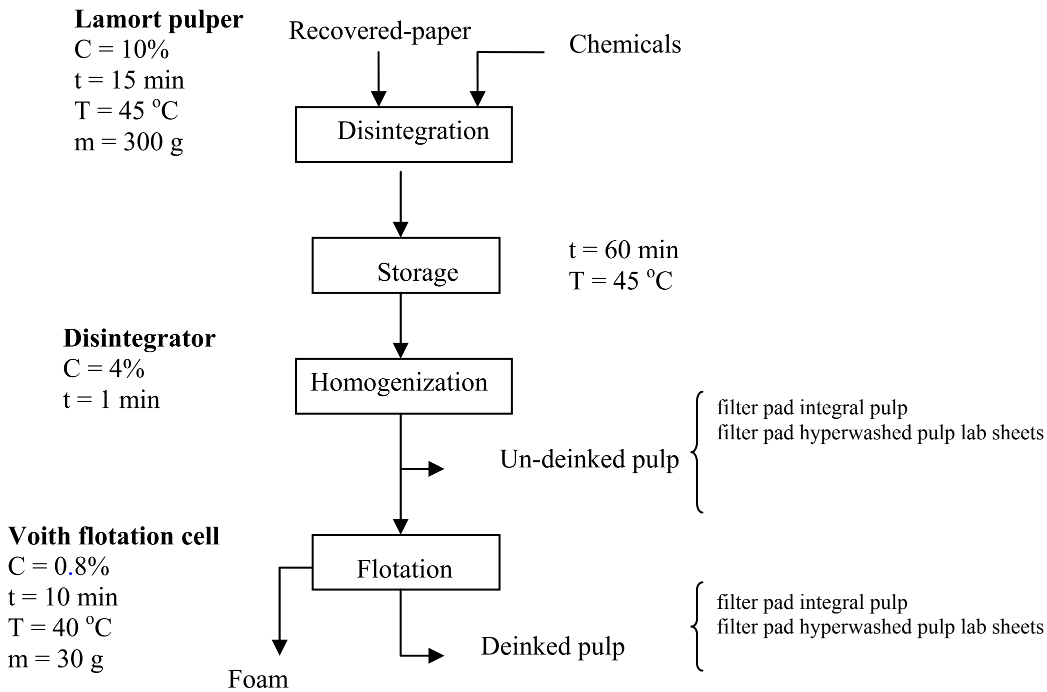

Figure 1: Working scheme and conditions of the deinkability test

To determine the filtrate characteristics (liquid phase extracted on a 150 µm mesh wire), a process water sample of 3000 g was centrifuged for 10 min, after which the resulting supernatant was analyzed.

Determination of quality characteristics

Determination on pulp

Optical characteristics, determined on an ERICLAB.8 – illuminant D 65, without UV radiation, observation angle 10^0 (8 measurements for each sample):

- brightness, [%]
- colour coordination: L^*, a^*, b^* [-]
- ERIC number, [ppm]
- reflectance at λ = 950 and 557 nm [%]
- ink eliminated at flotation (IE), [%]
- residual ink after hyperwashing in a vessel with a 105 µm sized bottom wire and water under a pressure of 100 bars (RI), [%]

Optical characteristics determined on a flat bed scanner with 600 dpi resolution, IBM PC Pentium III, image analyzing software Simpatic (PAPTECH):

- number of dark specks
- effective black area, [mm^2/m^2].

Ink elimination (IE) and residual ink (RI) were calculated according to the following formulas:

$IE = [(ERIC_{EPrepulped} - ERIC_{EPfloated})/ERIC_{EPrepulped}] X 100$

$RI = [ERIC_{EPrepulped} - ERIC_{HWDfloated})/ERIC_{EPrepulped}] X 100$

where: EP = entire pulp; HWD = hyperwashed pulp

Determination of filtrate charateristics

Chemical oxygen demand (COD) and turbidity were determined on LCK 514 phial (cuvette test with pre-loaded reactive) and on a LASA 20 Dr. Lange Photometer; cationic demand (CD) was measured on an automatic titration Mütek device; total solid suspension

(TSS) and dissolved material (DM) were oven-regulated at 100 °C; filter paper with 35 cm^3/min porosity was used.

RESULTS AND DISCUSION

Optical characteristics

The increase in brightness takes less notable values after flotation under alkaline conditions, for both digital and flexographic prints, while it becomes significant (15 points) for offset printed papers (Fig. 2).

The offset print (a mixture of newsprint and magazine) evidences the highest inorganic content (filler, coating), which increases the effectiveness of ink flotation. As shown in Figure 3, the ink previously present in the offset printing repulped material is removed at 91% efficiency. The efficiency in ink removal is expressed as the ERIC number for repulped, floated and hyperwashed materials.

Table 4 lists the ERIC numbers for the repulped and floated materials as entire pulp and hyperwashed materials. Apparently, after flotation, the ink content of the digitally printed paper stock remains almost at the same level as before (only a slight decrease from 22.6 to 19.3 ppm being recorded). The explanation lies in the cyan component of the printing ink, which gives the pulp a heavy blue colouration. As a consequence, the optical information given by the measuring device is slightly incorrect, for both brightness and ERIC number. Another disturbing factor could be the poor removal in the flotation of ink particles larger than 100 µm, which is the characteristic size for digital-print slurry. For digital-print deinked pulp, even hyperwashing generates unexpected results in brightness lowering. The explanation could be found in the efficient removal of the bright filler material and not of the much larger ink particles.

Researchers agree that this important problem of digital-print deinking, generating numerous ink particles above 100 µm, can be solved in two possible ways, and namely, by hot-dispersion, requiring an additional energy consumption of 180 kWh/t, and by enzymatic treatment.[5] Recent studies have evidenced a significant particle size reduction during a 0.0125% cellulase enzyme treatment in repulping, *i.e.* particles with sizes between 200 and 250 µm from 900 to 400 ppm, between 250 and 300 µm from 650 to 200 ppm and between 350 and 500 ppm from 1200 to 45 ppm, respectively, after flotation.[6] An insignificant decrease in ink concentration was also noticed in alkaline flexographic printings repulping, because the water-base flexographic ink dissolved in an alkaline environment gives a black aspect to the whole pulp. Even after flotation, the appearance of the stock does not change, due to a very poor separation of the hydrophilic flexo ink components. That is why, only a 1.5 point increase in brightness is observed.

Numerous studies reveal the low deinking ability of flexographic prints, *i.e.*, only a 15% flexographic print ratio in a mixture with offset prints drops brightness by about 10%, for both alkaline disintegrated and final pulp. Promising results have been obtained in the pilot repulping test with carboxymethyl cellulose or polyacrylic acid, applied for preventing ink re-deposition on the fibre surface.[7]

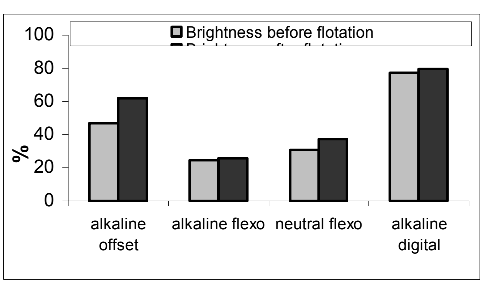

Figure 2: Evolution of brightness during flotation

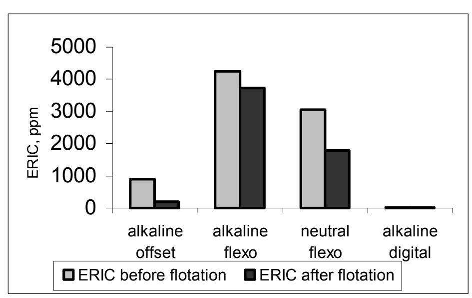

Figure 3: Evolution of effective residual ink concentration

Table 4
Determined and calculated values for repulped and floated pulp

Recovered paper and processing type	ERIC [ppm]				Ink eliminated, [%]	Residual ink, [%]
	Pulped Material		Floated material			
	Entire Pulp	Hyperwashed	Entire Pulp	Hyperwashed		
Alkaline offset	902.2	128	194.8	107.1	78.4	11.9
Alkaline digital	22.6	33.1	19.3	19.1	14.6	84.5
Alkaline flexo	4247.9	720.1	3721.7	753.5	12.4	17.7
Neutral flexo	3047.6	569.6	1790.4	669.9	41.3	22.0

Other works focus on the improvement of deinkability of flexographic prints through enzymatic treatments. Pulp treatment with 0.05% enzyme and 0.1% surfactant, performed under neutral conditions, may enhance[8] ink flotation from 10.7 to 38.6%.

A graphical comparison of the analyzed printings at different processing stages is presented in Figure 4, at a filter pad scan resolution of 118 pixels/cm.

The foam collected in digital print processing has a uniform size distribution, while the presence of much larger particles is obvious in flotation and hyperwashed pulp.

Flexographic print neutral deinking leads to much better flotation pulp appearance, comparative to the alkaline one.

The image analysis test results on the lab sheets are shown in Figures 5 and 6.

The observation may therefore be made that alkaline digital-print recycling without dispersion generates an impressive number of ink particles, which give not only a poor appearance to the deinked pulp, but also a huge number of oversized unremovable ink particles.

Image analysis measurements classify the identified black particles according to their size. Figure 9 shows the percent of particles, according to their size, in pulp disintegration and flotation.

Considerable differences are observed in the number of dark specks in digital and other print-type deinking (10-15 times higher in digital). The effective black area (shown separately, due to size differences) also shows 500-600 times higher values for digital printings, compared to the other three samples analyzed (Figs. 7 and 8).

It is obvious that, after the flotation stage, the particles larger than 40 μm record increased ratios in the stock, compared to those situated between 10 and 40 μm, the ratio of which dropped by 6%, suggesting the necessity of including a shredding stage in the deinking scheme for large ink particles, to enhance the characteristics of the final product.

Filtrate characteristics

Table 5 shows the results of the investigations performed on process water.

COD gives useful information on the environment impact and biodegradability of the dissolved and colloidal materials involved in the recycling system. The data from Table 4 indicate a heavily loaded process water in all alkaline systems. From this point of view, neutral flexographic-print deinking could be the best solution.

However, considering[9] the satisfactory optical characteristics of the pulp obtained in alkaline deinking and the possibility to close up the water loop (to reduce the fresh water consumption up to 5-15 m^3/t), the alkaline process may be judged as attractive and the most appropriate for several deinking systems.

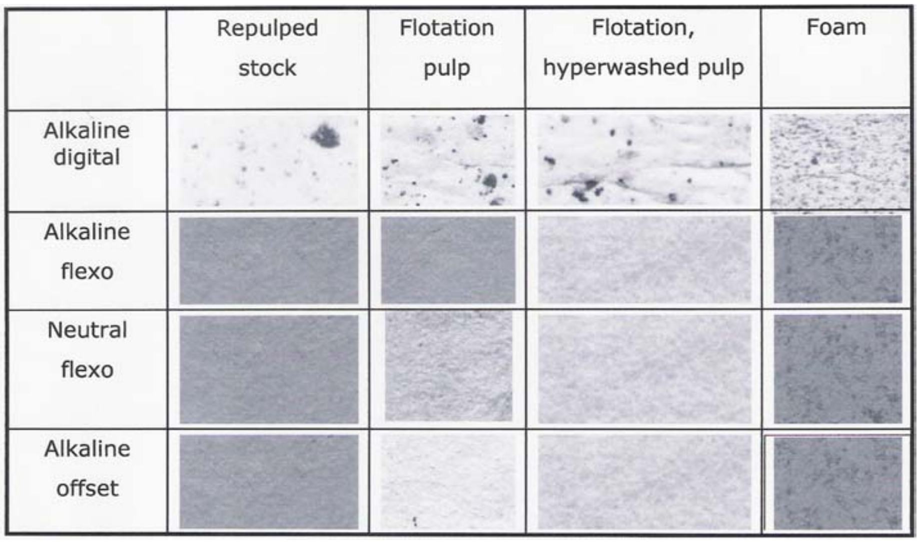

Figure 4: Graphical aspect of the analyzed printings at different processing stages

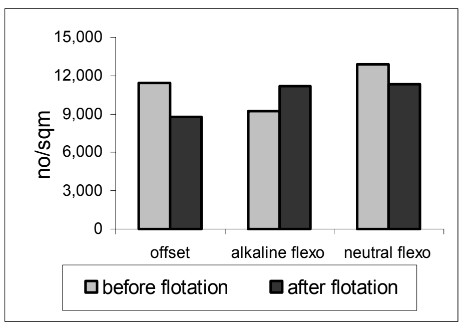

Figure 5: Evolution of dark specks in flotation

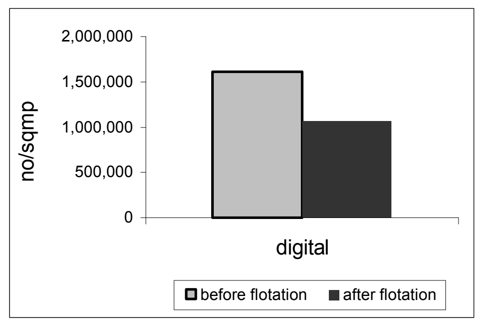

Figure 6: Evolution of dark specks of digital prints in flotation

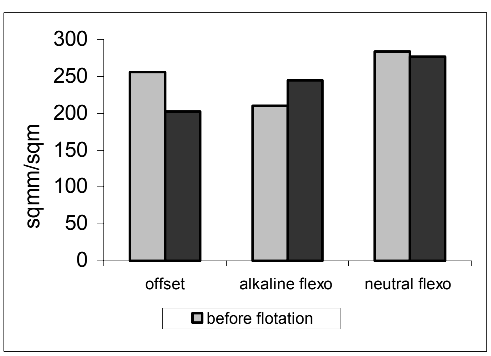

Figure 7: Evolution of effective black area during flotation

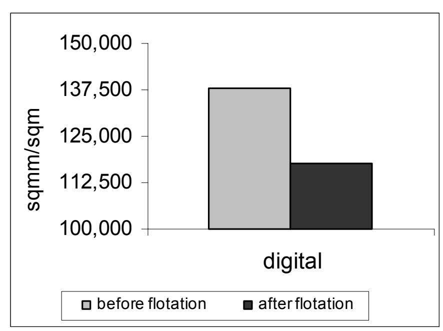

Figure 8: Evolution of effective black area for digital printing during flotation

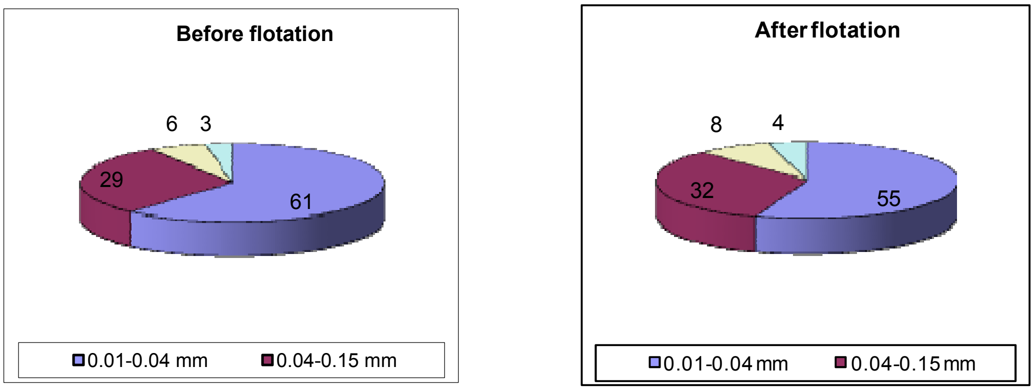

Figure 9: Size distribution of ink particles for digital printing

Table 5
Filtrate measurements

Parameter	Unit	Alkaline offset	Alkaline digital	Alkaline Flexo	Neutral flexo
COD (chemical oxygen demand)	mg/L	2 650	4 950	2 150	1 309
CD (cationic demand)	µeg/L	1.47	1.81	0.92	0.04
Dissolved material (MD)	g/L	3.8	n.d.	2.8	0.7
Total solid in suspension (TSS)	g/L	10.6	n.d.	3.68	1.49
Turbidity	FTU	23.6	355.0	maximum	144.7

CONCLUSIONS

- The optical characteristics of deinked pulp are critical as to choosing the best recycling method for the available wastepaper. The type of printing ink and solvent also plays an important role in recycled paper deinking.
- An ideal option for deinking could be the severe pre-screening of wastepaper by the type of print. However, this is not practical, therefore it is preferred to avoid the use of unidentified prints.
- Flexographic prints should not be processed by the alkaline method.
- Digital prints need a complex – chemical, enzymatic and mechanical – deinking treatment.
- The best way to process flexographic prints is by a neutral method, using a non-ionic surfactant as a unique deinking agent.
- For offset prints, alkaline deinking appears as the best solution as, under laboratory conditions, a 91% efficiency in ink detachment and an increase in brightness of up to 15 points can be obtained.
- It is strongly recommended not to mix the recovered paper printed by the flexographic method with the offset one. They should be first sorted at the collecting point and sent to the factories that use appropriate repulped methods for each kind of recovered paper.
- As to further improvements in deinking, the motto of the INGEDE Association is very appropriate: "When designing a print product, a good recyclability has to be a criterion".[10]

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