

The Deinkability Improvement of Offset Prints Made from a Two-Side Coated Substrate

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This paper describes the improved removal of impurities (coating, ink/toner) from offset prints produced by digital printing of two-side coated paper. The substrates were printed by conventional and digital offset processes. Based on image analysis results it was established that deinking flotation is an inefficient method for ink particle removal from digital offset printed paper, but it is efficient for ink removal from conventional offset printed paper. On the other hand, pre-treatment with hydrogen peroxide solution gives better results for ink particle removal from digital offset prints than from conventional offset prints. Optimal parameters for hydrogen peroxide pre-treatment for both offset prints were chosen based on unprinted substrate mass loss results in the preliminary investigation. These results showed that hydrogen peroxide pre-treatment is more successful at removal of impurities in comparison with flotation deinking without pre-treatment.

Keywords: Deinkability; Flotation deinking; Hydrogen peroxide pre-treatment; Two-side coated printing substrate; Conventional and digital offset prints

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INTRODUCTION

The importance of recovered paper as an essential raw material for the paper industry is huge. Offset printing is a widely used printing technique, and almost all recovered paper is printed by means of offset lithography and gravure processes. However, certain printing technologies (especially digital) have made deinking recycled paper more difficult (Carré and Magnin 2004). The deinking efficiency depends on printing method, printing substrate type, and printing ink chemical composition. The other influential factors are the kind and quantity of chemicals used in different phases of the deinking process, as well as deinking pH, deinking consistency, duration of each deinking operation, and the hydrodynamic factors of the flotation deinking process (Carre and Galland 2007). The deinking operation consists of two main phases:

- i) The detaching of the ink from the waste paper fibrous, carried out in a pulper generally with the addition of one or more chemical reagents;
- ii) The removal of the ink, after it has been detached from the pulp slurry by flotation or washing (Borchardt *et al.* 1998).

Flotation deinking is a successful method for removal of ink particles within a size range of approximately 20 to 300 μm in diameter (Heindel 1999). Failure to remove the larger ink particles results in unsightly dark or coloured specks in the recycled pulp.

Smaller particles that are not floated or washed from the pulp, whilst not visible to the naked eye, reduce the brightness (R_{457}) of the paper.

Recent studies in the field of digital printing and recyclability possibilities carried out at the Centre Technique du Papier (CTP) in France and at Papiertechnische Stiftung (PTS) in Germany indicated that inkjet inks are generally not deinkable, and thus incompatible with paper recycling (Caree and Galland 2007, Faul and Putz 2008, Faul and Putz 2009). Based on these findings INGEDE (the International Association of the Deinking Industry), who is dedicated to improving recyclability of recovered paper, initiated a dialogue with printer manufacturers to find some solution to this deinking problem. All the results completed up to this point have been well publicized at DRUPA (Vermaercke 2009) and are available to the public on the INGEDE official web page.

Digital printed material with dry toner (Xeikon, Kodak, or Xerox) can generally be deinked without difficulty (Doshi *et al.* 2009). By contrast, particularly poor deinking results were observed with water-based inkjet inks (Ben and Dorris 2011) and with liquid toner processes, such as that used by Indigo, which claims market leadership in digital colour printing systems (Carré *et al.* 2005, Fricker *et al.* 2007). These printers use fast-drying liquid inks (*e.g.*, ElectroInk), which mainly consist of petroleum hydrocarbon (> 70%) and resin coated pigments (< 15%) (Viluksela *et al.* 2010). The liquid toner is transferred from the blanket cylinder to the electrostatically charged paper, where it is fused to form a polymer film. When the printed paper is repulped at the beginning of the deinking process, these ink films result in large but very soft particles. These particles can neither be removed by the usual screens nor through flotation. The result is a high number of clearly visible dirt specks in the recycled paper (Fischer 2002).

Digital print processes can employ use coated papers to achieve a higher contrast and better print resolution. To get excellent print results, the paper surface is treated with the special coating (based on clay or chalk) and with other additives. Coating formulations and the amount of coating vary according to the paper type. A typical coating mix contains the following ingredients: 85% to 90% pigment (clay, calcium carbonate), 10% to 15% binding agent, and 1% to 2% additives. Properties such as smoothness, gloss, printability, and opacity generally improve with increasing coat weight (Anonymous).

The object of this study was to investigate the possibilities of separating and removing polymeric ElectroInk from a two-side coated substrate, one of the substrates recommended by the manufacturer of the printing machine. As commonly used flotation deinking conditions are inefficient for digital offset prints, we performed a preliminary investigation to improve the flotation deinking by a chemical pre-treatment process. From this preliminary investigation it was noticed that the best chemical for introduced pre-treatment for deinking flotation process is hydrogen peroxide.

EXPERIMENTAL

For this investigation, two-side coated matt art paper (130 g/m² grammage, 2.5% moisture and 24% ash) produced by Fedrigoni, Symbol Freelifa Satin, was used as the substrate for preparing digital and conventional offset prints. Digital offset prints were printed with an Indigo E-Print 1000+ press that uses special inks (CMYK) formulated for the digital process (Anonymous 2012). Conventional offset prints were made using a

Heidelberg Printmaster GTO 52-4(-P) device. All printed samples used in this investigation were printed over the entire surface. Three different investigations were performed to test the deinkability of printed samples: 1) flotation deinking without pre-treatment; 2) preliminary investigation for chemical pre-treatment; and 3) flotation deinking with hydrogen peroxide solution pre-treatment. Monitoring of deinkability efficiency was done through image analysis and ash content results. In this manner eight different samples were obtained for evaluation of the flotation deinking efficiency.

Image analysis was performed on handsheets made from digital and conventional pulp with and without pre-treatment, before and after flotation. These measurements were done using a Spec*Scan 2000 (Apogee Systems Inc.). Technical data about this software are: resolution 600 dots/inch, threshold 100 manual, and 256-shade Grayscale mode. All image analysis were performed on 6400 mm² of each handsheet surface to detect particle size in the range from 0.001 to >5 mm².

Ash content was determined by ignition at 920°C in Nabertherm Muffle Furnaces (according to TAPPI standard T4139).

1) Flotation Deinking Without Pre-Treatment

The chemical flotation deinking process flow is presented in Fig. 1.

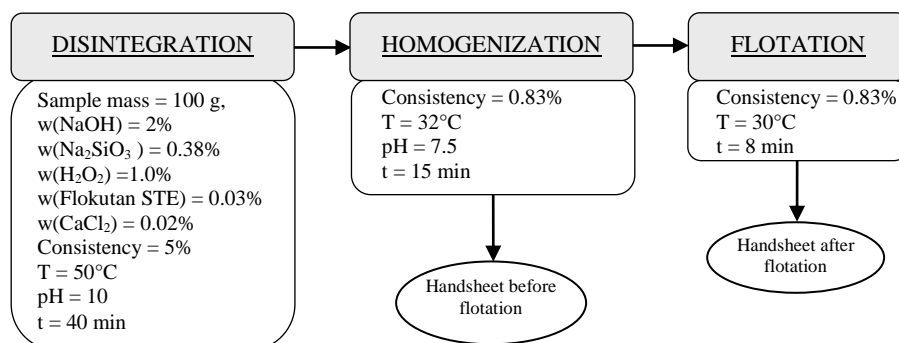


Fig. 1. Schematic presentation of the chemical flotation deinking process flow; pH is measured after each stage of chemical flotation deinking process by pH meter HACH Sension 378; w is chemical dosage related to oven dry sample

Flotation deinking (Fig. 1) was carried out using three main apparatuses: an Enrico Toniolo disintegrator, a laboratory flotation cell, and a laboratory handsheet former.

All trials were carried out by using 100 grams of printed sample. During disintegration, pulp slurry consistency and temperature were adjusted by adding 2 L of heated tap water, while the pH value was adjusted by adding NaOH to the suspension. Flokutan STE (Schill-Seilacher, Heilborn) was used as a deinking surfactant. H₂O₂, Na₂SiO₃, and CaCl₂ were added into the disintegrator, and after the defined disintegration time, the slurry was homogenised. The homogenization process conditions were adjusted by adding 10 L of tap water. The froth was manually removed from slurry surface in the flotation cell by spoon.

Handsheets dimensions 340 x 250 mm were made from pulps before and after flotation deinking using a laboratory handsheet former (Barbaric-Mikocevic *et al.* 2010). The obtained results of image analysis indicated inefficient ElectroInk particles removal from digital offset printed paper, so a pre-treatment process was introduced as an additional process for the deinking flotation method.

2) Preliminary Investigation for Chemical Pre-treatment

The control parameter for chemical pre-treatment efficiency was monitored only through sample mass losses for: a) conventional and digital offset prints and b) unprinted substrate. The printed and unprinted samples (dry mass of 1 g) used for each preliminary investigation were cut into 15 x 15 mm pieces.

a) Chemical agents

Pre-treatment of printed and unprinted samples refers to their soaking in distilled water (the first trial) and two different chemical agents (the second and third trial) and their subsequent washing with distilled water under stirring. The chemical agents used for soaking were sodium hydroxide at a solution pH 10 (the second trial) and hydrogen peroxide solution at a pH 10 and a concentration of 0.032 mol/L (the third trial). The pH value of hydrogen peroxide solution in the third trial was set using an NaOH solution of 5 mol/L concentration. These three trials were made for unprinted and printed samples under the same conditions (according to Fig. 2.).

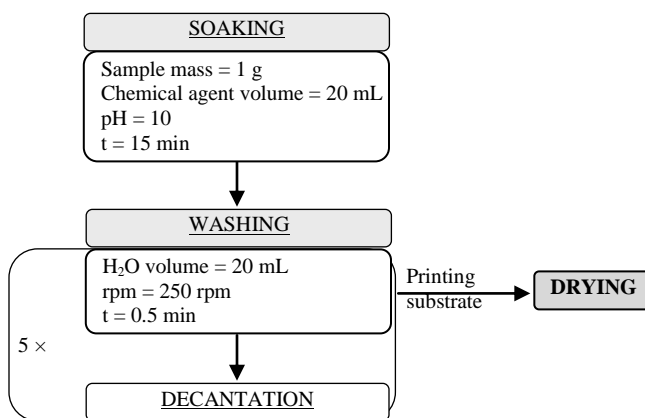


Fig. 2. Preliminary investigation workflow

The cut printed and unprinted samples were soaked (15 minutes) in a particular chemical agent solution at room temperature. Upon soaking, the sample was washed with distilled water, gradually in five steps (Fig. 2). Total washing time was 2.5 minutes (5×0.5 min). The purpose of sample washing was to remove separated particles (ink/toner and coating impurities) from the cellulose-mesh structure of the substrate. After the process water was decanted in the fifth washing step, scraps of the sample were placed on dry paper and blotted. The scraps were air-dried at room temperature and then dried in a desiccator.

Based on the best pre-treatment preliminary investigation results gained with H_2O_2 for unprinted and printed samples, it was decided to find the optimal parameters for that pre-treatment process.

b) Process conditions

As the interaction of printing substrate and printing technique have great influence on deinking efficiency, different conditions for the H_2O_2 pre-treatment process were applied only on unprinted two-side coated substrate. That chemical agent pre-treatment was investigated through monitoring the influence of hydrogen peroxide concentration (0.016, 0.032, 0.064 $\text{mol}\cdot\text{L}^{-1}$), soaking time (15, 60, 90, 120 min), and washing time (2.5, 3.5, 4.5, 5.5 min) on unprinted substrate mass losses. For that purpose, three groups of experiments were prepared (Table 1). In each group, one process parameter was changed while the others remained the same.

Table 1. Experimental Process Conditions (t_s = soaking time; t_w = washing time)

| Experimental group | $c(\text{H}_2\text{O}_2)$, $\text{mol}\cdot\text{L}^{-1}$ | t_s , min | t_w , min |
|--------------------|--|-------------|-------------|
| 1. | 0.016 | 15 | 2.5 |
| | 0.032 | | |
| | 0.064 | | |
| 2. | 0.032 | 15 | 2.5 |
| | | 60 | |
| | | 90 | |
| | | 120 | |
| 3. | 0.032 | 15 | 2.5 |
| | | | 3.5 |
| | | | 4.5 |
| | | | 5.5 |
| | | | |

From the results for the first experimental group, the highest mass loss was obtained for 0.032 H_2O_2 concentration, so that concentration was chosen for further experimental work. From the second and third experimental groups, the optimal parameters for washing (2.5 min) and soaking (15 min) time were obtained. Optimal parameters for flotation deinking with hydrogen peroxide pre-treatment for both offset prints were chosen based on unprinted substrate mass loss results in the preliminary investigation.

3) Flotation Deinking With Hydrogen Peroxide Solution Pre-Treatment

Oven-dried offset print samples of 100 g torn into approximately 15×15 mm pieces were soaked in a beaker for 15 minutes in 1 L hydrogen peroxide ($c = 0.032$ $\text{mol}\cdot\text{L}^{-1}$, pH 10) at room temperature, without stirring. After the soaking time had expired, the sample was washed in a 5 L separator with tap water for 15 minutes (Fig. 3).

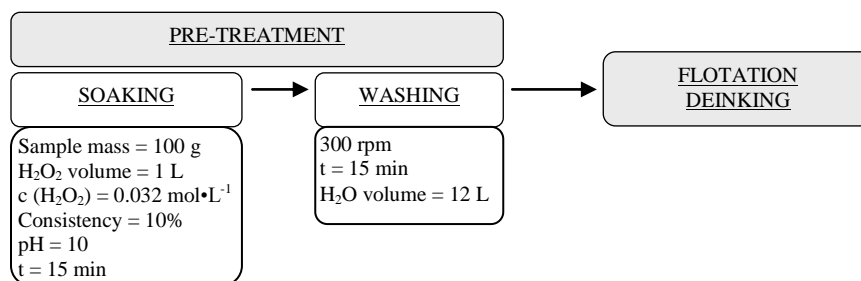


Fig. 3. Workflow of offset prints pre-treatment before flotation deinking

As show in Fig. 4, a separator was used during the washing process to improve detachment of impurities from fiber slurry. The separator was placed into a vessel of 15 L volume, into which 12 L of tap water was added. An agitator device set at 300 rpm was placed into the separator (Fig. 4). The separator bottom, made of a sieve with 5 x 5 mm pores, is lifted from the bottom of vessel. This setup provides separation of detached impurity particles from separator to vessel.

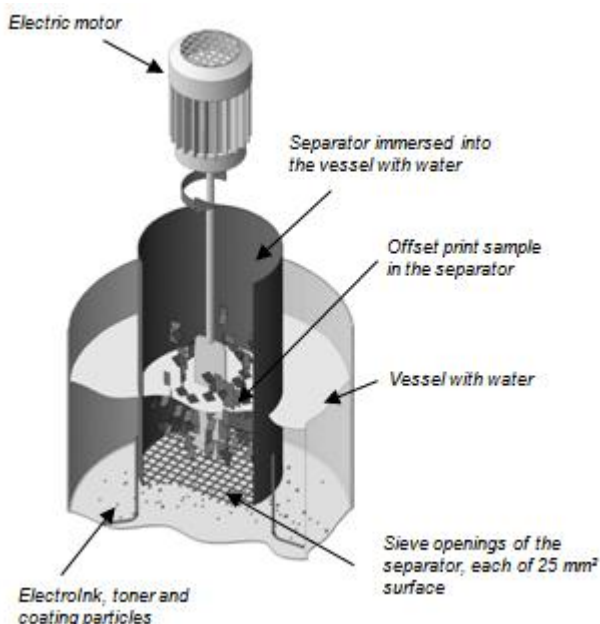


Fig. 4. Schematic presentation of separator for washing in pre-treatment process with hydrogen peroxide

Polymeric ElectroInk particles, conventional offset print ink particles, and coating particles from printing substrate were driven by stirring through sieve openings from the separator into the outer vessel. When the washing time had expired, the separator was taken out of the vessel, and substrate scraps were transferred from the separator into the disintegrator for flotation deinking according to Fig. 1.

RESULTS AND DISCUSSION

Flotation Deinking Without Pre-Treatment

The deinkability of digital and conventional offset prints made on two-side coated substrate was monitored through image analysis results (Table 2) for handsheets before and after flotation.

Image analysis was performed on the 6400 mm² handsheet surface to detect particle size in the range from 0.001 to >5 mm². All gained image analysis data were converted into relative results on unit area (1 cm²).

Table 2. Handsheets Image Analysis Results (Flotation Deinking without Pre-treatment)

| Particle Size Classes, mm ² | Digital Offset Print | | | | Conventional Offset Print | | | |
|--|---------------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|
| | Before flotation | | After flotation | | Before flotation | | After flotation | |
| | particle number per 1 cm ² | particle area per 1 cm ² | particle number per 1 cm ² | particle area per 1 cm ² | particle number per 1 cm ² | particle area per 1 cm ² | particle number per 1 cm ² | particle area per 1 cm ² |
| 0.001 - 0.006 | 25.14 | 0.07 | 37.30 | 0.11 | 47.25 | 0.00 | 1.69 | 0.00 |
| 0.006 - 0.013 | 9.50 | 0.09 | 13.73 | 0.13 | 20.41 | 0.19 | 0.47 | 0.00 |
| 0.013 - 0.021 | 3.34 | 0.06 | 4.59 | 0.08 | 7.45 | 0.12 | 0.22 | 0.00 |
| 0.021 - 0.03 | 2.39 | 0.06 | 2.83 | 0.07 | 3.20 | 0.10 | 0.09 | 0.00 |
| 0.03 - 0.04 | 1.19 | 0.04 | 2.31 | 0.08 | 1.94 | 0.07 | | |
| 0.04 - 0.05 | 0.58 | 0.03 | 0.92 | 0.04 | 0.58 | 0.37 | 0.02 | 0.00 |
| 0.05 - 0.06 | 0.84 | 0.05 | 1.20 | 0.06 | 0.28 | 0.00 | | |
| 0.06 - 0.07 | 0.44 | 0.03 | 0.95 | 0.06 | 0.16 | 0.00 | | |
| 0.07 - 0.08 | 0.39 | 0.49 | 0.48 | 0.04 | 0.08 | 0.00 | | |
| 0.08 - 0.09 | 0.23 | 0.02 | 0.38 | 0.03 | 0.02 | 0.00 | | |
| 0.09 - 0.10 | 0.19 | 0.02 | 0.27 | 0.03 | 0.05 | 0.00 | | |
| 0.10 - 0.15 | 0.67 | 0.08 | 1.06 | 0.13 | 0.06 | 0.00 | | |
| 0.15 - 0.2 | 0.34 | 0.06 | 0.59 | 0.10 | | | | |
| 0.20 - 0.25 | 0.27 | 0.06 | 0.45 | 0.10 | | | | |
| 0.25 - 0.3 | 0.13 | 0.03 | 0.42 | 0.12 | | | | |
| 0.30 - 0.40 | 0.34 | 0.11 | 0.39 | 0.14 | | | | |
| 0.40 - 0.60 | 0.28 | 0.13 | 0.16 | 0.00 | | | | |
| 0.60 - 0.80 | 0.30 | 0.53 | 0.23 | 0.16 | | | | |
| 0.80 - 1.00 | 0.13 | 0.12 | 0.20 | 0.19 | | | | |
| 1.00 - 1.5 | 0.22 | 0.27 | 0.14 | 0.17 | | | | |
| 1.5 - 2.00 | 0.06 | 0.71 | 0.03 | 0.05 | | | | |
| 2.0 - 2.5 | 0.13 | 0.28 | 0.06 | 0.13 | | | | |
| 2.5 - 3.0 | 0.03 | 0.08 | 0.03 | 0.09 | | | | |
| 3.0 - 4.0 | 0.11 | 0.39 | 0.02 | 0.49 | | | | |
| 4.0 - 5.0 | 0.09 | 0.43 | 0.02 | 0.07 | | | | |
| >5.0 | 0.16 | 1.46 | 0.03 | 0.42 | | | | |
| Total | 47.48 | 4.30 | 68.81 | 2.49 | 82.41 | 0.69 | 2.47 | 0.02 |

ElectroInk particles are detected in a wide range of sizes (0.001 to >5 mm²), while conventional offset ink particles were approximately of uniform size (0.001 to 0.15 mm²). The total particle number per 1 cm² of conventional ink particles was reduced from 82.41 to 2.47, which is in accordance with a decreasing of total particle area per 1 cm² from 0.69 to 0.02. On the other hand, no decreases were observed for digital ElectroInk particles after flotation. Moreover the particle number per 1 cm² of analysed particles after flotation was considerably higher (68.81) in comparison to the particle number per 1 cm² before flotation (47.48), while total particle area per 1 cm² of those particles was decreased from 4.30 to 2.49. The increase of total ElectroInk particles number after flotation was based on efficient flotation of particles larger than 1 mm². After their removals from the suspension, particles smaller than 1 mm² were identified in the handsheet made after flotation. Before the flotation, these particles were likely covered-up by larger particles, so they could not have been identified. The handsheets area occupied by particles after flotation also indicated better flotation efficiency for conventional ink particles.

As we can see from Table 2, gained image analysis results are influenced by the printing technique on chosen printing substrate. During digital printing, the liquid ElectroInk polymerizes on the printing substrate. The polymer particles obtained by

disintegration and defibering of such prints have irregular shapes and a wide range of sizes (Fig 5). From our experimental results, it was evident that deinking flotation primarily removes particles larger than 1 mm^2 , which is not in agreement with the flotation efficiency literature data. Flotation deinking is reported to remove particles of 0.015 to 0.150 mm^2 (Somasundaran *et al.* 1999) or of 0.010 to 0.100 mm^2 (Borchardt 1994). Laser-printer prints investigations showed that particles from 0.040 to 0.120 mm^2 can be efficiently removed by flotation (Walmsley *et al.* 1997).

On the other hand, flotation efficiency of conventional offset print particles was much better. During conventional offset printing, solvent from ink penetrates into the substrate, while the pigments and the resins remain on the surface. Sodium hydroxide and hydrogen peroxide hydrolyzed and saponified these resins. So, deinking chemical agents play an important role during ink disintegration of conventional offset prints. Separated conventional ink particles were smaller, more regular shape (digital camera photography Fig. 5), with a negative charge on their surface, which facilitates their flotation.

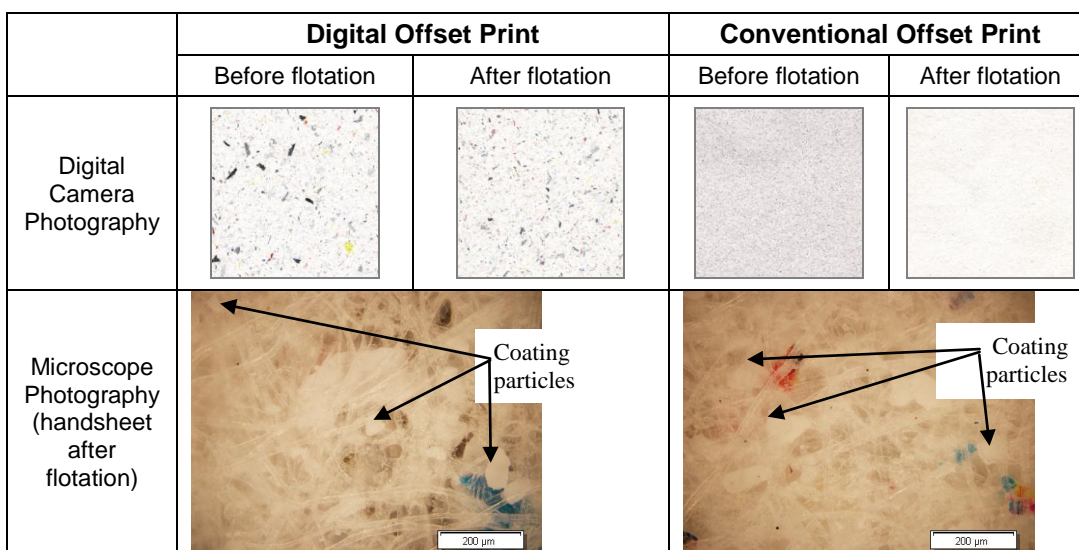


Fig. 5. Handsheets photography taken by digital camera and Olympus Metallurgical Microscope BX51, magnification 20x

Figure 5 shows representative images of coating particles in handsheets after offset print flotation between fibres viewed with the 20x magnification of an Olympus Metallurgical Microscope BX51. Particles from the paper substrate coating are also considered to be impurities, and these were not efficiently removed by flotation.

Due to the inefficiency of the deinking of ElectroInk and paper substrate coating particles, it was necessary to conduct additional experiments to improve deinkability by a chemical pre-treatment process.

Preliminary Investigation for Chemical Pre-Treatment Conditions

a) Chemical agents

Chemical pre-treatment included the soaking of unprinted and offset print samples in distilled water and chemical agents (NaOH and H_2O_2) and washing (Fig. 2).

Table 4. Mass Loss of Samples after Treatment with Different Chemical Agents

| Sample: | Mass Loss, % | | |
|---------------------------|-------------------------------|------|-----------------------------------|
| | H ₂ O ₂ | NaOH | H ₂ O _{dist.} |
| Unprinted substrate | 31.6 | 27.5 | 23.2 |
| Digital offset print | 30.4 | 18.6 | 13.8 |
| Conventional offset print | 25.7 | 12.5 | 11.1 |

Table 4 shows mass losses of unprinted substrate samples and of offset prints after pre-treatment in distilled water, sodium hydroxide solution, and hydrogen peroxide solution. Among all used solutions for all three used samples, the highest mass loss was observed in the case of the hydrogen peroxide solution pre-treatment. The highest mass loss for unprinted substrate (31.6 %) explains higher mass loss values for digital offset prints (30.4 %) than for conventional (25.7 %), which can be attributed to the different printing techniques. Coating particles from the digital offset print residue are glued together by the ElectroInk polymerized resins, while this was not the case for conventional offset print residue. Conventional offset prints soaked in hydrogen peroxide solution resulted in lower mass losses compared to mass losses of digital offset prints, which correlated with samples appearances (Fig. 6).

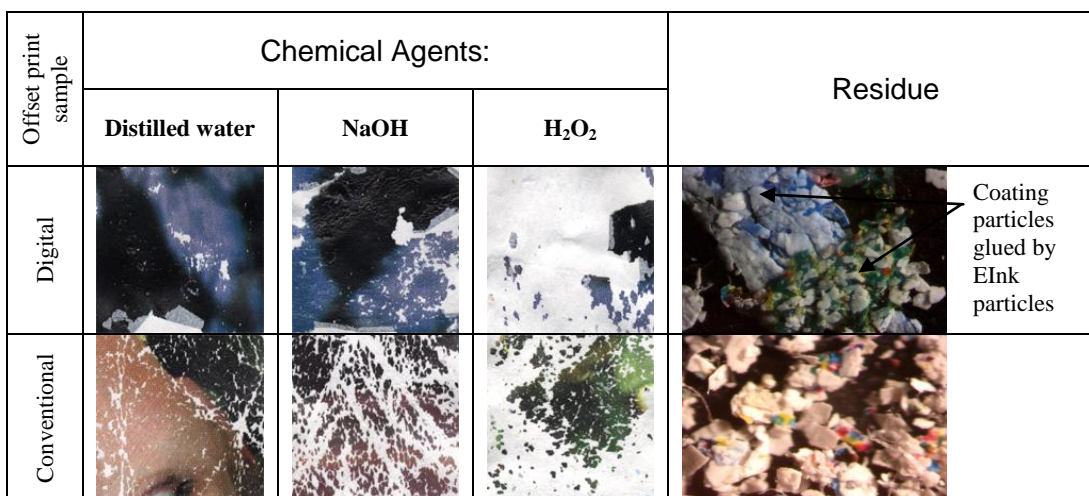


Fig. 6. Offset print samples and residues after treatment by different chemical agents. An optical microscope (Leitz, Orholux) was used to visualise residue particles removed from the offset printed samples.

b) Process conditions

Optimal soaking (t_s) and washing time (t_w) for hydrogen peroxide pre-treatment were established according to Table 1 on unprinted two-side coated substrate since both offset print methods were carried out with the same matt art paper.

In Fig. 7 for all three charts, a zero value of the x-coordinate corresponds to an untreated dry sample (mass 1g). Increasing the hydrogen peroxide concentration (Fig. 7a) led to the highest substrate mass losses, while increasing the soaking (Fig. 7b) and washing time (Fig. 7c) intervals did not have a significant influence on substrate mass losses.

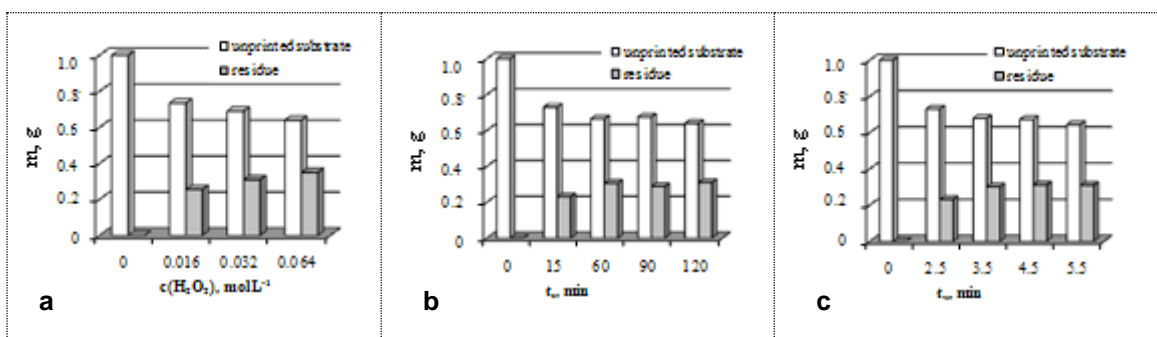


Fig. 7. The influence of: a) hydrogen peroxide concentration, b) soaking and c) washing time on unprinted two-side coated substrate mass loss, *i.e.* residue mass

Based on the results of preliminary investigation on unprinted substrates, the following chemical pre-treatment conditions were selected: ($t_s = 15$ min; $t_w = 2.5$ min). Further pre-treatment efficiency investigations on digital and conventional prints, for different hydrogen peroxide solutions (0.016, 0.032, and 0.064 mol/L) concentrations, were done (Table 5).

Table 5. Digital and Conventional Offset Prints Pre-treatment Efficiency in Different Hydrogen Peroxide Concentrations

| $c(\text{H}_2\text{O}_2)$, mol L ⁻¹ | Unprinted Substrate | Digital Offset Print | | Conventional Offset Print | |
|--|------------------------|---|-----------------|---|-----------------|
| | Mass loss, g | Sample appearance after treatment | Mass loss, g | Sample appearance after treatment | Mass loss, g |
| 0.016 | 0.265 | | 0.253 | | 0.193 |
| 0.032 | 0.316 | | 0.304 | | 0.257 |
| 0.064 | 0.350 | | 0.320 | | 0.261 |

An unsatisfactory amount of polymeric ElectroInk was removed during the treatment of digital offset prints in the H_2O_2 solution of 0.016 mol/L concentration. Cracks were noticeable on the surface of polymeric ElectroInk. Increasing the peroxide concentration to 0.032 mol/L caused the ElectroInk to peel off from the printing substrate, but it was not completely detached and removed by washing. The lower side of the peeled ElectroInk, which was in contact with the printing substrate, was white due to the coating particles glued to ElectroInk (Table 5). The coating and ElectroInk were separated together from the printing substrate. Treatment in peroxide solution of 0.064 mol/L concentration resulted in complete removal of ElectroInk from the printing substrate.

A large amount of the remaining print could be seen on samples of conventional offset print after the treatment regardless of the hydrogen peroxide concentration. In contrast to ElectroInk particles, conventional ink particles were not efficiently removed from the print substrate by the pre-treatment. Increasing the peroxide concentration from 0.016 to 0.064 mol/L led to an increase in the mass loss of the unprinted substrate from 0.265 to 0.350 g, of the digital offset print from 0.253 to 0.320g, and of the conventional offset print from 0.193 to 0.261g (Table 5).

Flotation Deinking with Pre-treatment

Based on the obtained results, flotation deinking of offset prints pulps was carried out after their pre-treatment under established optimal process conditions ($t_s = 15$ min, $t_w = 2.5$ min, $c(\text{H}_2\text{O}_2) = 0.032$ mol/L) (Fig. 3). Table 6 shows the ash content of the handsheets before and after flotation for both types of offset prints with and without pre-treatment, while Table 7 shows particle size distribution for those handsheets as determined by image analysis.

Table 6. Ash Content of Handsheets Before and After Flotation, for Both Types of Offset Prints Without and With Pre-Treatment

| Offset print | Ash Content, % | | | |
|--------------|-----------------------|-----------------|--------------------|-----------------|
| | Without pre-treatment | | With pre-treatment | |
| | before flotation | after flotation | before flotation | after flotation |
| Conventional | 20.69 | 16.65 | 8.61 | 7.70 |
| Digital | 21.44 | 17.38 | 8.75 | 7.79 |

Handsheets formed before and after flotation deinking with pre-treatment were compared with handsheets formed without pre-treatment in terms of ash content (Table 6), particle size distribution, and total area covered (Table 7). The ash content in the handsheets before flotation was higher compared to the handsheets after flotation and was independent of printing technique, because the inks from both types of offset print consist of organic compounds. All inorganic material that was detected by ignition at 920°C originated from the two-side coated substrate. The results of handsheets ash content for both offset print (Table 6) indicate negligible decreasing of coating particles by flotation in flotation deinking process without hydrogen peroxide pre-treatment (approximately decreasing for 4.0%). In the flotation deinking process with hydrogen peroxide pre-treatment, the flotation efficiency for coating particle removing was negligible (approx. 1.0%).

The importance of hydrogen peroxide pre-treatment process was observable as a notable decrease of ash content of both offset print handsheets before flotation made after flotation deinking process with hydrogen peroxide pre-treatment. The handsheets without pre-treatment had ash content of approximately 21% and the handsheets with pre-treatment had 8.7% for both types of prints, which means significant decreasing of ash amount (approximately 12.0%). So, the highest removal of coating particles was achieved in pre-treatment stage of flotation deinking process with hydrogen peroxide solution pre-treatment.

Table 7. Image Analysis Results for Handsheets Formed After Flotation Deinking with Pre-Treatment (Fig. 4)

| Particle Size Classes, mm ² | Digital Offset Print | | | | Conventional Offset Print | | | |
|--|---------------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|
| | Before flotation | | After flotation | | Before flotation | | After flotation | |
| | particle number per 1 cm ² | particle area per 1 cm ² | particle number per 1 cm ² | particle area per 1 cm ² | particle number per 1 cm ² | particle area per 1 cm ² | particle number per 1 cm ² | particle area per 1 cm ² |
| 0.001 - 0.006 | 2.53 | 0.01 | 1.17 | 0.00 | 1.59 | 0.01 | 0.42 | 0.00 |
| 0.006 - 0.013 | 0.72 | 0.01 | 0.20 | 0.00 | 0.75 | 0.01 | 0.08 | 0.00 |
| 0.013 - 0.021 | 0.20 | 0.00 | 0.06 | 0.00 | 0.23 | 0.00 | 0.03 | 0.00 |
| 0.021 - 0.03 | 0.17 | 0.00 | 0.08 | 0.00 | 0.14 | 0.00 | 0.03 | 0.00 |
| 0.03 - 0.04 | | | 0.02 | 0.00 | 0.06 | 0.00 | | |
| 0.04 - 0.05 | | | 0.02 | 0.00 | | | | |
| 0.05 - 0.06 | 0.02 | 0.00 | 0.05 | 0.00 | 0.02 | 0.00 | | |
| 0.06 - 0.07 | 0.08 | 0.01 | | | | | | |
| 0.07 - 0.08 | 0.02 | 0.00 | | | | | | |
| 0.08 - 0.09 | 0.03 | 0.00 | 0.03 | 0.00 | | | | |
| 0.09 - 0.10 | 0.02 | 0.00 | | | | | | |
| 0.10 - 0.15 | | | 0.02 | 0.00 | | | | |
| 0.15 - 0.2 | | | 0.03 | 0.01 | | | | |
| 0.2 - 0.25 | | | 0.02 | 0.00 | | | | |
| 0.25 - 0.3 | | | | | | | | |
| 0.30 - 0.40 | 0.03 | 0.01 | 0.03 | 0.01 | | | | |
| 0.40 - 0.60 | 0.02 | 0.01 | 0.02 | 0.01 | | | | |
| 0.60 - 0.80 | | | | | | | | |
| 0.80 - 1.00 | 0.03 | 29.56 | | | | | | |
| 1.00 - 1.5 | | | 0.02 | 23.19 | | | | |
| 1.5 - 2.00 | 0.03 | 58.47 | | | | | | |
| 2.0 - 2.5 | 0.02 | 36.13 | 0.02 | 35.81 | | | | |
| 2.5 - 3.0 | | | | | | | | |
| 3.0 - 4.0 | 0.02 | 53.14 | | | | | | |
| 4.0 - 5.0 | 0.02 | 68.27 | | | | | | |
| > 5.0 | 0.03 | 273.30 | | | | | | |
| Total | 3.97 | 570.88 | 1.77 | 102.09 | 2.80 | 22.44 | 0.56 | 0.00 |

Image analysis of the handsheets prior to flotation had 3.97 particles per 1 cm² for the treated digital offset print and 2.80 particles per 1 cm² for the conventional offset print. After flotation 1.77 particles per 1 cm² were present in the handsheet obtained from the digital offset print pulp and 0.56 particles per 1 cm² in the handsheet obtained from the conventional offset print (Table 7), which is in correlation with the total particle area decreasing for both types of offset prints.

CONCLUSIONS

Results of flotation deinking studies for digital/conventional offset prints on two-side coated substrates indicated the following:

1. Flotation deinking, the most commonly applied process in paper recycling, does not efficiently remove polymeric ElectroInk particles from digital offset prints, but represents an efficient procedure for ink removal from conventional offset prints.
2. Substrate coating particles in digital/conventional offset prints pulp are impurities that cannot be removed by flotation. Additional pre-treatment processing before deinking

flotation is necessary for efficient coating particles removal from two-side coated substrate and consequently ink particles, especially ElectroInk from digital offset print.

3. The best chemical for offset prints pre-treatment used in our investigation is hydrogen peroxide solution, which is detected through mass losses/residual mass of unprinted and printed samples.
4. The efficiency of flotation deinking process with hydrogen peroxide pre-treatment was validated by significant decreases of:
 - a) ElectroInk particles in digital offset print handsheets detected through image analysis;
 - b) Substrate coating particles in both offset prints handsheets detected through ash amount.

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