VOLUME – II

- SUBJECTS -

LIQUID AND GASEOUS EFFLUENT TREATMENT
LIQUID EFFLUENT TREATMENT
METHODS OF WASTE TREATMENT
MONITORING AND CHARACTERIZATION
MUNICIPAL WASTES
PLASTICS AND PAPERS
PRECIOUS AND RARE METALS
RECOVERY OF NON-FERROUS METALS
RECYCLING OF FERROUS METALS
-REWAS’04-
GLOBAL SYMPOSIUM
ON RECYCLING,
WASTE TREATMENT
AND CLEAN
TECHNOLOGY

VOLUME – II

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INFLUENCE OF DIGITAL PRINTS AGEING ON PROCESS RECYCLING OF WASTE PAPER

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Abstract

Recycled fibres have become greater and more important source of raw materials in graphic paper production. The efficiency of this method depends on the technique and printing conditions, kind of ink and kind of printing substrate.

Except the mentioned, the type and amount of chemicals used in processing stages, hydrodynamics of process, pH, pulp consistency, time of disintegration, slushing method and other chemical and physical operating conditions influence the efficiency of deinking operation.

In the investigations presented in this work, the samples of multicolour digital and conventional offset prints were used. The prints were naturally and accelerated aged before deinking flotation. Some characteristics of the optical values before and after flotation were observed on handsheets. The investigation results show that natural ageing of prints influences the handsheet brightness, deinkability respectively. This influence is greater with conventional offset prints with the ink with greater ration of renewable raw materials. With handsheet after disintegration of the accelerated aged prints of digital offset printing, the decrease of the particle size and smaller increase of handsheet brightness can be noticed by the increase of ageing time. The investigation results show greater change of relative reflection of handsheet before and after deinking flotation in the function of accelerated ageing.
Introduction

Recycled papers are today a very important raw material resource. Deinking is a process for detaching and removing printing inks from prints. The efficiency of this method depends on the technique and printing conditions, kind of ink and kind of printing substrate[1-3].

Each technology places different demands on the ink and particle size, and ink and toner chemistry determine effectiveness of deinking chemicals. The particle sizes of water based flexo inks are in the range 0,2 -1,0 μm after repulping and so they are too small for flotation. Because the ink is hydrophilic it can not be agglomerated by collector chemicals [4, 5]. Water based rotogravure inks behave similarly to water based flexo inks [6]. Ultraviolet inks and varnishes form hard polymers are difficult to break up in the disintegrator and these particles may be too big to flotate. Resins used in toner for laser printing and photocopying make them difficult to detach from the fibres. When the toner is removed from the substrate, during repulping, the toner fused film is detached in flat plate-like structures. These particles are too big to be removed successful by flotation [7].

Except the mentioned, the type and amount of chemicals used in processing stages, pH, pulp consistency, time of disintegration, shushing method and other chemical and physical operating conditions influence the efficiency of deinking operation [8, 9]. Many authors study the hydrodynamics of the flotation and washing processes [10, 11]. One of the problems here is the detachment efficiency and removal of ink particles [12]. Bradel J. i others study the quality of the waste water and the technological purification [13].

Other consideration in deinkability of waste paper includes pulp ageing. This term could be in fact defined as the sum of all irreversible physical and chemical processes which happen in the material during time. Deterioration in quality of an aged paper can manifest itself in chemical permanence and the decrease in mechanical durability. The permanence of paper depends on the chemical resistance of its components and of the influence of external factors. The durability depends mainly on the physical and mechanical characteristics of the raw materials, impact of microclimatic factors such as heat, humidity or emanation and on contamination by ions and gas from the environment and action of microorganisms [14, 15].

Acid hydrolysis of cellulose and related carbohydrates is one of the most important factors responsible for the degradation of paper during ageing. It is well know that strength loss of paper during accelerated ageing increases linearly with the partial pressure of oxygen. [16]

Other processes that lead to paper degradation are alkaline hydrolysis, thermolysis, and physical – mechanical damage and attack of microorganisms and mould.

Many authors were occupied with investigations of recycling efficiency of natural and accelerated aged prints. In this area the reduction in the deinked pulp brightness change in other recycled paper properties, and change in process water after recycling of waste paper exposed to ageing during the summer months, defined as a summer effect were studied [17]. The conclusion is that the summer effect is due to the ageing or thermal drying of printing inks. This drying will lead to
the increased ink fragmentation (more ink to remove) and ink attachment (ink can not be separated from the fiber chemical or flotation mechanism).

Ryu and others studied the influence of natural and accelerated ageing primarily on flexographic prints and on those made in offset printing technique with the inks of different chemical composition applying the process of alkaline and neutral chemical deinking. [18]. These results showed that neutral deinking would provide significant improvement in brightness, yield and freeness as compared with conventional alkaline deinking. Before treatment the samples were hurriedly aged 24 hours at 105° C. Allese V. et al. presents a deinking procedure suitable for waste paper with a high content of flexographic newspaper using a modified alkaline flotation process [19]. The material was aged for three months before each trial. Detachment of printing ink from different types of aged paper was investigated by Sjostrom et al [20].

The influence of the natural and accelerated ageing of prints of digital and conventional offset printing in regard to the efficiency of alkaline deinking flotation has been investigated in this work. The results of optical measurements of handsheet after disintegration and flotation in dependence on the kind of substrate and characteristics of the process itself have been discussed.

**Experimental**

The samples of multicolour prints were obtained by the digital offset printing with liquid toner ElectroInk (Indigo E-Print 1000+ printing machine) and with conventional offset printing (Heidelberg sheet fed machine) The unique test form was used in printing. The prints were made on the uncoated and coated paper.

In the process of conventional printing the model inks were used, composed of components presented in table 1.

<table>
<thead>
<tr>
<th></th>
<th>Composition of the model ink1 (%)</th>
<th>Composition of the model ink 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyd resin</td>
<td>10,0</td>
<td>10,0</td>
</tr>
<tr>
<td>Hard resin</td>
<td>0</td>
<td>21,0</td>
</tr>
<tr>
<td>Pigment</td>
<td>17,0</td>
<td>17,0</td>
</tr>
<tr>
<td>Additives</td>
<td>13,0</td>
<td>13,0</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>26,5</td>
<td>0</td>
</tr>
<tr>
<td>Vegetable oil</td>
<td>5,0</td>
<td>39,0</td>
</tr>
<tr>
<td>Modified colophony resin</td>
<td>28,5</td>
<td>0</td>
</tr>
</tbody>
</table>

One series of prints was naturally aged in the period from 35, 70, 105, 140, 175 and 210 days and the other was aged accelerated in the chamber at 80° C and relative humidity of 65% in the period of 10, 20, 30 and 40 days.

Samples prepared in such a way were used in the process of alkaline deinking flotation; the process flow is presented schematically in figure 1.
In the phase of sample soaking, deinking chemicals *1% hydrogen peroxide, 0,4% surfactant, 0,2% DTPA, 1% sodium hydroxide and 1% sodium silicate (were added. The consistency is 10% in regard to the dry substance. A good mixing action was achieved. The disintegration stage was continued for 45 minutes. Suspension was diluted to 0,6% pulp consistency. An optimum level of hardness was maintained in the flotation cell from 200 ppm CaCO₃. The flotation time was eight minutes.

The handsheets were made using a laboratory sheet former, according to standard method T 205. Brightness was determined by using the standard method ISO 2469.

Other optical methods were performed by X-Rite spectrophotometer with the support of ColorShop program. The measuring results were processed by means of Data Analysis program and technical Graphic Origin Professional.

**Results And Discussion**

The parameter most frequently used to evaluate the optical quality of deinked pulp is the spectral reflectance factor R₄₅⁷, used as brightness. Figure 2 presents the results of handsheet brightness
obtained after deinking flotation of the naturally aged prints of the conventional and digital offset printing.

Figure 2. Brightness of handsheet after deinking flotation of the naturally aged prints

As it is visible from the measuring results of the prints before recycling the value of handsheet brightness is decreased in dependence on the time of prints exposing to that process. Except that, the influence of dependence of handsheet brightness on the printing technique as well as chemical composition of the used ink can be recognized. Greater influence on the decrease of handsheet brightness in relation to the duration of the ageing process in comparison to the results obtained with model ink 1 or with ElectroInk can be noticed by deinking flotation of print made with model ink with greater ratio of renewable raw materials (model ink 2). Almost uniform negligible decrease of brightness without oscillations in the observed period can be noticed with handsheets obtained by deinking flotation of the aged digital offset prints.

The ageing effect could be explained by observing it as the continuation of the ink drying on the printing substrate. The drying effect of the conventional offset ink with greater ration of mineral oil happens by adsorption with oxidation and lasts longer, four to six months. [21].

Vegetable based offset inks significantly changed in structure undergo oxidation reaction. In this reaction the following steps are included by a free radical: oxygen reacts slowly with the oil to form hydperoxides, after that decomposition of hydroperoxides and propagation of the radicals follow and at the end the termination of free radicals with formation of cross links come. [22].

In the digital offset printing the liquid ElectroInk used pigments are similar to those in conventional offset inks., it acts electrostatically and dryes very quickly . In drying process ElectroInk is laminated into an ink-plastic film. The ink and film are peeled off the blanket and
applied to the paper with the help of the transfer oil. ElectroInk dries to a film for transfer from the blanket, before it reaches the substrate. The ElectroInk does not penetrate into the paper [23].

These drying principles of prints are recognizable as the defined influence on brightness, i.e. deinkability of the printed prints in the function of ageing. The obtained differences in handsheet brightness are in the range less than one unit which gives the clear picture about the efficiency of detaching and removing of ElectroInk from prints.

The difference of handsheet brightness before and after deinking flotation is presented in figure 3.

![Graph showing brightness differences](image)

Figure 3. Difference of handsheet brightness before and after deinking flotation of the accelerated aged prints of the digital offset printing

It is visible from the results that there are not essential differences in the handsheet brightness increment in the experimental conditions in relation to the accelerated ageing of digital offset prints. Handsheets after deinking flotation of prints of digital offset printing submitted to accelerated ageing are presented in figure 4.
The observed prints in this case were accelerated aged for 10, 20, 30 and 40 days in the chamber at 80°C and 65% of humidity without the influence of radiation. As it is visible from the presented results the duration of the ageing process has the impact on the particles size of ElectroInk, so that they decrease with time. The influence on the particle size of ElectroInk in the deinking flotation process more noticeable in our earlier investigations, were caused by the conditions in the printing process itself (by changing the voltage on the drum) as well as with usage of different model of printing machines for digital offset printing in combination with different printing substrates [3, 24].

The results of relative reflections of handsheet before and after deinking flotacije are presented in figure 5.
Relative reflections of handsheet before and after deinking flotation for prints of digital offset printing which were accelerated aged for 10 days (5a) and 40 days (5b) are presented in figure 5. The values of reflections of spectral curves point at the difference of the optical properties of handsheet during the whole measuring area of wave lengths. In both cases the increased reflection in the area from 425 to 430 nm can be seen, which is the consequence of addition of optical whitening agents during the production of the original paper. The increase of relative reflection of handsheet after deinking flotation of prints which were accelerated aged for 40 days in relation to the handsheet before flotation is an interesting data. Such data point at the positive influence of the recycling process in the context of improved surface properties of handsheet. However, such trend was not registered during processing of digital offset prints aged for shorter time, e.g. for 10 days.
Conclusion

On the basis of the obtained investigation results in the frame of experimental condition it could be concluded that natural ageing of prints influences the brightness of handsheet, i.e. the deinkability. This influence is somewhat greater with conventional offset prints with the ink with greater ratio of renewable raw materials. With handsheet after disintegration of the accelerated aged prints of the digital offset printing the decrease of the particle size and smaller increase of brightness increment was noticed with the increase of the ageing time.

The investigation results show greater change of relative reflection of handsheet before and after deinking flotation in the function of accelerated ageing.

The performed investigations are the contribution to the explanation of the influence of ageing of digital offset prints in the context of the process of detaching and removing printing inks during the recycling of paper in relation to the prints of the conventional offset printing. Practical application of the investigations is interesting in the production of the recycled papers especially in the case of temperature changes during the summer period.

The obtained results points at the necessity of further investigations of influential parameters of the recycling process itself in the mixture of the real sample.

References


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