Influence of Deinked Pulp on Paper Colour and its Susceptibility to Ageing

Abstract
The dyeability of chemical pulp and deinked pulp (DIP) as well as a mixture of these grades with cationic direct dyes were investigated. It was found that the paper obtained contains significant quantities of fluorescent whitening agents (FWA), which were added to white printings to increase their brightness. When using FWA, there are problems obtaining the colour of dyed paper required. The fluorescence of a whitening agent fades away after exposure to light. The faster fading of paper containing recycled fibres reflects lower penetration of a dye into fibres in comparison to primary fibres. The use of deinked pulp in the manufacture of colourfull papers is expected to grow. For this reason paper mills will be forced to use expensive bleaching technologies to remove FWA from deinked pulp. This indicates that the need to obtain a very high level of brightness in printing papers with FWA is ungrounded.

Key words: chemical pulp, deinked pulp, DIP, colour, dyeing, direct dyes.

Table 1. Fibre composition and chromacity of the model pulps.

<table>
<thead>
<tr>
<th>Pulp Nr.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre composition:</td>
<td>bleached hardpulp</td>
<td>bleached softpulp</td>
<td>DIP (deinked pulp)</td>
</tr>
<tr>
<td>ISO Brightness, %</td>
<td>70.8</td>
<td>51.3</td>
<td>-</td>
</tr>
<tr>
<td>CIE Whiteness</td>
<td>74.4</td>
<td>51.0</td>
<td>67.3</td>
</tr>
<tr>
<td>CIE Tint</td>
<td>46.0</td>
<td>-3.2</td>
<td>-2.34</td>
</tr>
<tr>
<td>Chromacity coordinates:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L*</td>
<td>96.0</td>
<td>92.47</td>
<td>87.81</td>
</tr>
<tr>
<td>a*</td>
<td>-0.22</td>
<td>0.38</td>
<td>+0.12</td>
</tr>
<tr>
<td>b*</td>
<td>+2.69</td>
<td>6.63</td>
<td>+5.3</td>
</tr>
<tr>
<td>Colour difference ΔE* with reference to white standard</td>
<td>4.8</td>
<td>10.0</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Table 1 were used. The yellow cationic direct dye Pergasol Gelb F-6GZ fl. (CIBA Specialty Chemicals Inc.) was used for dyeing. Only the cationic direct dye was used in the research. Nowadays, dyes of this type are the most frequently used for paper due to the good dyeing level of various pulp grades, including recycled pulps of non-homogeneous composition. Auxiliary agents were not used purposely.

Methodology of sample preparation
The beating of primary fibres was carried out in laboratory conditions, in a Valley beater to a freeness of 40 °SR according to Standard PN-ISO 5264-1:1999. The recycled pulp was then dissolved in water. The dye was added to a 2.5% pulp suspension at a temperature of approx 20 °C, with a pH of approx. 7.5. The contact time of dyeing substances with the pulp amounted to 10 minutes. The Pulp suspension was used to form paper sheets of approx. 75 g/m², using Rapid – Köthen apparatus according to Standard PN-EN ISO 5259-2:2001, and then they were calendered using a two-roll laboratory calendar with/at a pressure of 1000 kPa.

Introduction
Deinked pulp (DIP - waste paper from which printing ink has been removed) is an important fibrous raw material in the production of printing papers. To produce bright deinked pulp, manufacturers use printed graphic papers, mainly white grades which have to go through the deinking process to remove printing ink. Printing inks cannot be entirely removed without the application of specific bleaching processes, which is why this pulp grade has a slightly grayish shade. The grayness of deinked pulps can be reduced by bleaching, but their fluorescence poses a serious problem. The fluorescence is developed by FWA added to white publication and office papers to raise their whiteness. Present recycling methods cannot remove FWA entirely from the pulp, which is why all deinked pulp based papers show fluorescence. Even gray sanitary papers of the poorest quality demonstrate fluorescence in UV light. The presence of FWA in deinked pulp poses a serious problem connected with metamerism, specifically in the case of dyed papers [1]. The fluorescence level of recycled pulps is variable and depends on the grade of paper they are made of. For this reason it is difficult to maintain identical colour (both white and chromatic) in large manufacturing batches [2].

This research focused on examining the impact of DIP pulp content on paper colour.

Materials
For the purpose of this research, model pulps of the composition presented in Table 1 were used. The yellow cationic direct dye Pergasol Gelb F-6GZ fl. (CIBA Specialty Chemicals Inc.) was used for dyeing. Only the cationic direct dye was used in the research. Nowadays, dyes of this type are the most frequently used for paper due to the good dyeing level of various pulp grades, including recycled pulps of non-homogeneous composition. Auxiliary agents were not used purposely.
Before testing, the samples were conditioned according to Standard PN-EN 20187:2000.

Colour parameters were determined with SpectroEye apparatus (GretagMacbeth) (illuminant D65, observer 10°) according to the following standards: PN -EN ISO 105-J01 ; 2002, ISO 2470:1999 and PN-ISO 11475:2002.

Light resistance was determined by exposing the samples on Xenotest apparatus according to Standard PN-ISO 105-B02: 1997/Ap 1:2002. Due to the significant differences in the resistance to light between the samples tested, colour modification was tested after a five-hour-exposure (resistance to light in ISO scale – aprox 3).

Results

Significant differences were observed in the light reflectance curves of paper sheets made of model pulp 1 (chemical pulp) and model pulp 3 (recycled pulp) (Figure 1). Paper sheets made from model pulp 1 reflected more light in the yellow range but less in the blue than sheets from model pulp 3. The Characteristic maximum in the range of blue colours on the light reflectance curve visibly shows the presence of the fluorescent whitening agent in the deinked pulp (pulp 3).

At wavelengths longer than 480 nm, pulp 3 had low light reflectance coefficients, more or less equal in the whole range, which is connected with the gray colour developed by residual quantities of the print ink. In model pulp 2, the optical properties of pulp 1 and pulp 3 are summarised. Light reflectance coefficients for this pulp in the blue range were higher than in the case of pulp 3 but lower than for pulp 1. All the light reflectance curve in the wavelength range longer than 480 nm run between the curves for pulp 1 and pulp 3.

The fluorescence of the whitening agent disappeared after the light exposure of sheets made of model pulp 2 and 3 (Figure 2), whereas the grayness caused by residual amounts of print ink remained. The colour shifted towards yellow (Figure 2) and the brightness decreased significantly. The ISO brightness for model pulp 1 was practically unchanged, whereas in the case of pulp 2, it decreased by 13.5% and approx 14% for model pulp 3 (Figure 3).

In papers coloured with yellow cationic direct dyes, the increased content of recycled pulp decreased colour saturation as a result of the addition of dye colour, the FWA which remained in the pulp, the graying effect caused by residual amounts of print ink (decreased light reflectance in the yellow range) as well as the lower dyeability of recovered fibres (Figure 4). Therefore the use of recovered paper posed some problems in the attempt to obtain the required paper colour.

The light resistance of the dyed samples decreased proportionally with the increased content of recycled pulp. The colour faded and shifted towards an achromatic colour. The brightness lessened proportionally with the higher content of recycled pulp in the paper sheet (Figure 5).

Easier colour fading of recycled pulp-based-paper proves that there is lower penetration of the dye into recycled fibres than into primary fibres. Colour fading and its modification were connected with the fact that a larger amount of radiant quantum energy was reaching the surface of the fibres. The dye molecules collided more often with the falling light, passing to an excited state, richer in absorbed radiation energy. The molecules in
an excited state reacted more easily with their surroundings (mainly with oxygen from the air), changing their structure and ability to absorb visible radiation. Colour modification arose due to changes in the molecules of fluorescent whitening agents present in the recycled pulp.

**Summary**

The amount of FWA in paper recovered from white printing papers depends on the type and origin of such papers, which is why we can never be certain that the colour of paper containing this sort of pulp will meet expectations. This can be problematic, especially when manufacturing dyed papers. In the coming years utilisation of deinked pulp in the production of colourful/coloured papers will grow, and the paper industry will be forced to use expensive bleaching technologies to remove FWA from deinked pulp. This indicates that the need to obtain a very high level of brightness in printing papers with FWA is ungrounded.

**References**
