Introduction
The pulp and paper industry constantly seeks new, environmentally–friendly technologies, amongst others, by:
- increasing the share of annual agricultural plants in the manufacture of paper,
- continuously increasing the use of waste paper pulp in the manufacture of paper [1].

Secondary fibres are valuable feedstock for the paper industry, constituting about one third of the total amount of raw materials used, which is due to favourable prices, when compared to primary fibrous pulp, and as a result of waste paper recycling promotion in many European countries.

However, the addition of certain amounts of primary fibres is often needed to arrive at the expected strength and optical properties of the paper. The average recovery rate of waste paper amounts to ca. 43% in Europe and 37% in Poland. In 2006, the total amount of waste paper used in Poland was 1021 thousand tons [1 - 3].

Various types of waste paper pulp with different fibre compositions are used in the manufacture of paper. Presently, in paper making a distinct tendency can be seen toward the use of white mixed office waste (MOW) mainly from ink-and laser printers and copiers. MOW is a large source of valuable paper fibres which, after deinking and bleaching, can be used in the manufacture of high quality paper and sanitary tissues [4 - 5].

Bleaching has to fulfil two basic functions:
- removal of residual lignin from the pulp,
- eliminate the various dyes introduced during papermaking [6].

Presently, the use of elemental chlorine in the ECF bleaching process (Elementary Chlorine Free) is banned for ecological and hygiene reasons. Moreover, in the production of hygiene tissues, any chlorine-containing compounds must be eliminated, including chlorine dioxide. Such processes are named TCF (Totally Chlorine Free) [7, 8]. Hence, the challenge is to replace traditional and very effective bleaching media with much less active oxygen substances like oxygen, ozone and hydrogen peroxide. This tendency occurs both in primary fibre pulp and in all types of waste paper pulp for the manufacture of white paper.

The bleaching power of hydrogen peroxide and other peroxy compounds is limited due to quick decomposition of the substances. In fact, even traces of bivalent cations of transition metals like iron, manganese and copper catalyse the decomposition of hydrogen peroxide and other peroxy compounds like peroxide acetic acid. Catalysing metal ions may issue from the MOW itself or be delivered by the process water and equipment used for deinking and multi-stage bleaching. The metal ion content varies greatly in waste paper pulp, depending on the type: the content of iron ion ranges between 100 to 170 mg/kg, manganese ion from 1 to 6 mg/kg and copper from 10 to 50 mg/kg.

High temperature (above 90 °C) accelerates the decomposition as well. On the other hand, high temperature is a positive factor as it speeds up the consumption of hydrogen oxide using less bleaching agent and provides better brightness in a very short time [5, 9 - 11].

In the bleaching of deinked waste paper pulp (as in the bleaching of groundwood), particularly in closed water loops, a serious problem arises caused by the hydroxy- peroxide consuming two enzymes: catalase and peroxidase. The bacteria-generated enzymes are most active at the usual deinking temperature i.e. 50 °C; their deactivation only occurs beyond 70 °C. It is therefore recommended to conduct the bleaching of deinked waste paper pulp at 90 °C or higher.

Table 1. Properties of the waste paper pulp used in the investigation.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Kappa number</th>
<th>Brightness, %</th>
<th>yellowness, %</th>
<th>Ash content, %</th>
<th>Content of metal ions, mg/kg</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 1</td>
<td>59.9</td>
<td>55.2</td>
<td>10.7</td>
<td>8.90</td>
<td>15.7</td>
<td>37.1</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td>Batch 2</td>
<td>63.1</td>
<td>61.1</td>
<td>26.1</td>
<td>9.66</td>
<td>15.3</td>
<td>37.7</td>
<td>26.3</td>
<td></td>
</tr>
</tbody>
</table>

Key words: waste paper pulp, bleaching peroxide, compound.
The elements capable of inhibiting the growth of bacteria, resulting in the too fast decomposition of $\text{H}_2\text{O}_2$, are peroxy compounds containing peracetic acid and hydroxy peroxide itself at proper process conditions [12-14].

**Objective and scope of the investigation**

The investigations were made within the research grant entitled “Bleaching of deinked waste paper pulp by means of peroxy and enzymatic materials” with the aim of applying hydroxy peroxide and other peroxy compounds, which proved effective in the delignification and bleaching of high-yield sulfate pulp, to the bleaching of waste paper pulp [15].

The introductory research presented herein includes the bleaching of waste paper pulp after deinking by means of:

- hydroxy peroxide ($\text{P}$) with the addition of its stabilisers: magnesium sulfate ($\text{MgSO}_4$) and ethylenediaminetetraacetic acid (EDTA),
- peroxy compounds: peracetic acid ($\text{CH}_3\text{COOOH}$), dimethylooxirane (DMD),
- hydroxy peroxide enhanced by the addition of activators: tetraacetyleneylendiamine (TAED), cyanamide ($\text{CN}$) and ammonium molybdate ($\text{(NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \times 4\text{H}_2\text{O}$).

**Methodology**

**Bleaching of the waste paper pulp**

A weighed portion of the waste paper pulp (calculated on absolute dry matter) was introduced into a glass reactor equipped with an agitator, situated in an oil bath. The bleaching proceeds at a pulp concentration of 12, 20 and 25%, at 80 - 90 °C. After each bleaching step, the pulp was squeezed out to reclaim the bleaching liquor. Next, the pulp was washed with tap and distilled water. The washing was continued until a neutral reaction took place. From the washed pulp, sheets for testing were formed in a Büchner funnel.

**The residual bleaching substance** was determined in accordance with a published method [16].

**The brightness of the waste paper pulp**

was tested in accordance with Standard ISO 2470:1999.

**Results**

**Enhancing the bleaching power of hydrogen peroxide using stabilisers that inhibit its decomposition**

Chelating agent ethylenediaminetetraacetic acid (EDTA) and magnesium sulfate ($\text{MgSO}_4$) were used to remove transition metal cations from the pulp, thus decreasing the destabilising the impact of the metals upon the hydrogen peroxide.

It was found that $\text{H}_2\text{O}_2$ was most effectively stabilised by $\text{MgSO}_4$, where the bleaching liquor had a concentration of 0.2%, and the EDTA of 0.1%.

In the experiments it appeared that the most profitable efficient mix of stabilisers is composed of $\text{MgSO}_4$ and EDTA, which are introduced into the bleaching liquor in the amount of 0.2% and 0.1%, respectively. The addition of stabilisers slowed the decomposition of hydrogen peroxide at 90 °C down, whose residual content after bleaching was in the range of 0.27 – 1.53%, depending on the bleaching time (Figure 1). The result was a brightness increase for both pulp batches after a processing time of as little as 60 minutes. In batch 1 the brightness increase was 5% and 7% for a pulp concentration of 12% and 20%, respectively, while in batch 2 it was 3% on average for both concentrations. Prolonging the bleaching time to 120 and 180 minutes resulted in a brightness increase by 1% and 2%, respectively, for batch 1 pulp but with no positive change in the case of batch 2 pulp (Figure 2).

Considering the favourable brightness levels of 63.3% and 64.5% attained at 20% pulp concentration, an attempt was made to increase the pulp concentration to 25%. The result was poor: brightness dropped by 3% for the two batches when compared to the trials with 20% pulp concentration (Figure 3 see page 114). The considerable decrease in brightness can be explained by the possibility of insufficient mixing of the pulp with chemicals in the course of the bleaching process.

**Improving the bleaching effects of waste paper pulp with hydrogen peroxide by the addition of stabilising agents**

The bleaching of waste paper pulp with peracetic acid in a slightly acetic medium
The use of a blend of persulfuric and peroxy compounds means of bleaching of waste paper pulp by Enhancing the hydroxy peroxide when compared to bleaching without the use of the dose (60 – 70%) peroxide decomposition, reflected by a 2 -3% increase of 2 -3% compared to trials without the Q step. (Figure 6). Also observed was an inhibition of the hydroxy peroxide decomposition, reflected by a much lower use of the dose (60 – 70%) when compared to bleaching without the Q step, in which no residual amount of the peroxide was actually observed.

Enhancing the hydroxy peroxide bleaching of waste paper pulp by means of peroxy compounds

The use of a blend of persulfuric and peracetic acids (PXA), and the last acid alone as bleaching agents increasingly brings to attention the bleaching of waste paper pulp containing unbleached fibres. Despite high bleaching potential, peroxy compounds do not deteriorate mechanical properties and their efficacy is an asset in the removal of ink traces and other impurities remaining in the pulp after deinking, whereby they ease further bleaching with hydrogen peroxide. Peroxy acids can particularly be helpful in the removal of impurities originating from office paper, and effectively assists in the bleaching of waste paper pulp with low lignin content [17].

The high content of lignin and ash content of about 9% in the types of waste paper pulp investigated (kappa number above 60) made bleaching with non-delignifying agents like hydroxy peroxide difficult.

Peracetic acid and mixed peracetic acid (PXA) were used to enhance the bleaching and de-delignifying action of peroxide in the bleaching of waste paper pulp

The bleaching of sulfate pulp in neutral medium with peroxy acid is a proven process yielding favourable results [18]; hence, it seemed adequate to employ similar bleaching conditions for treating waste paper pulp. In the case of peracetic acid (Pa), which was used for the bleaching of batch 2 pulp, various amounts of sodium hydroxide (NaOH) (1.5 - 3.0%) and liquid glass (NaSiO3) (0.4 - 3.0%) calculated as an absolute dry pulp mass were applied. Other process conditions were following: a temperature of 60 and 80 °C, a time of 60 - 150 minutes, a pulp concentration of 15 and 20%, the amount of Pa introduced 0.5 - 1.0% calculated as H2O2

The introduction of Pa to the first bleaching step increased the pulp’s brightness only slightly (on average by 3%) in relation to the initial value. Better brightness results could be achieved for bleached pulp using Pa concentrations of 20% (time 60 min) and 0.5%, calculated for an absolute dry pulp. In some of the trials (No. 68, 88, Table 2), a brightness de-

**Figure 3.** Comparison of H2O2 bleaching effectiveness of waste paper pulp with dependence on pulp concentration; 3% H2O2, 0.2% MgSO4, 0.1% EDTA, 0.3% NaOH, pH ≈ 10.5, 90 °C, 180 min.

**Figure 4.** Exhaustion of hydrogen peroxide after the bleaching of waste paper pulp with peracetic acid with dependence on the reaction medium; (1% Pa as H2O2, 0.5%MgSO4, time 60 min, pulp conc. 20%).

---

**Table 2. Bleaching of waste paper pulp with peracetic acid Pa; *0.2% EDTA.**

<table>
<thead>
<tr>
<th>Trial No (Batch 2 pulp)</th>
<th>Pulp conc., %</th>
<th>Time, min</th>
<th>Temp., °C</th>
<th>Pa amount as H2O2, %</th>
<th>N2SiO3 amount, %</th>
<th>NaOH amount, %</th>
<th>pHx</th>
<th>Brightness, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial waste paper</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>61.0</td>
</tr>
<tr>
<td>67</td>
<td>20</td>
<td>60</td>
<td>80</td>
<td>1.0</td>
<td>---</td>
<td>2.0</td>
<td>4.31</td>
<td>62.0</td>
</tr>
<tr>
<td>68</td>
<td>20</td>
<td>60</td>
<td>80</td>
<td>1.0</td>
<td>---</td>
<td>3.0</td>
<td>4.48</td>
<td>63.0</td>
</tr>
<tr>
<td>70</td>
<td>20</td>
<td>150</td>
<td>60</td>
<td>1.0</td>
<td>---</td>
<td>3.5</td>
<td>4.62</td>
<td>65.2</td>
</tr>
<tr>
<td>71</td>
<td>15</td>
<td>150</td>
<td>60</td>
<td>1.0</td>
<td>---</td>
<td>3.5</td>
<td>4.54</td>
<td>66.8</td>
</tr>
<tr>
<td>72</td>
<td>15</td>
<td>150</td>
<td>60</td>
<td>1.0</td>
<td>---</td>
<td>2.0</td>
<td>4.28</td>
<td>66.9</td>
</tr>
<tr>
<td>73</td>
<td>15</td>
<td>150</td>
<td>60</td>
<td>1.0</td>
<td>---</td>
<td>1.5</td>
<td>4.17</td>
<td>67.0</td>
</tr>
<tr>
<td>88</td>
<td>20</td>
<td>60</td>
<td>80</td>
<td>1.0</td>
<td>0.43</td>
<td>1.5</td>
<td>4.31</td>
<td>61.2</td>
</tr>
<tr>
<td>89</td>
<td>20</td>
<td>60</td>
<td>80</td>
<td>0.5</td>
<td>3.0</td>
<td>0.8</td>
<td>5.15</td>
<td>66.0</td>
</tr>
<tr>
<td>90*</td>
<td>20</td>
<td>60</td>
<td>80</td>
<td>0.5</td>
<td>0.43</td>
<td>0.8</td>
<td>5.10</td>
<td>66.8</td>
</tr>
</tbody>
</table>
crease of up to 4% was observed in relation to the initial value. Such a distinct drop in brightness was probably caused by an insufficient amount of NaOH introduced into the process. Somewhat better results were observed for bleaching with Pa in slightly acidic medium at an initial pH of 7 - 7.5. (see p. 32.) It is the reverse to what proceeds in the bleaching of sulfate pulp [18].

Mixed peracetic acid (PXA) composed of persulfuric and peracetic acids proved more effective than peracetic acid in the bleaching. An amount of 0.5 - 0.7%, calculated as active oxygen, was introduced into the waste paper pulp. This addition not only resulted in a brightness increase (average 5%) but also in a reduction in the kappa number by 10 units to the level of 52.9% (batch 2 pulp) (Figure 7).

Addition of activators to enhance the bleaching of waste paper pulp with hydrogen peroxide

For hydrogen peroxide to have a more effective bleaching action, it is advisable to convert it into a form in which the so-called “active oxygen” (AO) plays a dominant role. AO is formed under the action of suitable activators which are added directly to the peroxy step.

In the investigations presented, several hydrogen peroxide activators were used in the bleaching of waste paper pulp, notably TAED, which is applied as an optical whitening agent in quality washing powders, dimethylooxirane (DMD), cyanamide (P\(_{CN}\)), which reacts with H\(_2\)O\(_2\) to produce a transition form – peroxyimido carboxylic acid, which is a compound of higher activity than peroxide, and hydrogen peroxide activated by ammonium molybdate - P\(_{akt}\) ((NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\) \(
\times 4\)H\(_2\)O), which, having been introduced into the peroxy step (P\(_{akt}\)), forms an active peroxy complex [18 – 21] in the slightly acidic medium (pH ~ 5). It is known from professional literature that the addition of activators in the peroxy bleaching of pulp enables to substantially limit the amount of peroxide used in the process, meaning better utilisation [22, 23].

In the course of the research, optimal conditions were selected for the bleaching of waste paper pulp with the use of the above-mentioned named materials. The use of 1% DMD as AO at 20% pulp concentration and temperature of 50 °C for 60 minutes resulted in a brightness increase of 1 – 2%. The subsequent hydroxy peroxide bleaching added a further increase of 2% on average.

As a hydrogen peroxide activator, 500 ppm of ammonium molybdate was introduced into the bleaching of waste paper pulp as molybdenum calculated as an absolute dry pulp. The process was run in slightly acidic medium (pH ~ 5). The use of the activator did not improve the pulp’s brightness, which even slightly decreased. The effect can be explained by the high content of inorganic matter in the pulp (above 8%), which prevented the formation of active complexes of hydroxy peroxide and ammonium molybdate.

An increase in brightness was observed when another activator – cyanamide (P\(_{CN}\)) was introduced directly into the peroxy step. An average brightness of 63% was achieved in the two-step bleaching (P\(_{CN}\)P). Tetraacetyldiamine (TAED) was the next activator introduced directly into the peroxy step. Its bleaching activity was higher compared with that of the above-mentioned activators; an average brightness of 64% was attained. Further bleaching with hydroxy peroxide caused the brightness to increase to the level of 66.8% (Figures 8 and 9, see page 116).
Conclusions
From the introductory investigations presented, the following conclusions can be drawn:

- The use of stabilisers capable of inhibiting the decomposition of hydroxy peroxide and other peroxide-containing compounds caused the brightness of waste paper pulp to increase from 55.1% (batch 1) and 61.0% (batch 2) to an average of 65%

- The introduction of active peroxo substances and activated hydroxy peroxide greatly eased the bleaching of waste paper pulp, in spite of a high lignin content (the kappa number being above 60 units)

- From amongst the active forms of hydroxy peroxide presented, the best results were achieved with a mix of peracetic acid (PXA) and peracetic acid (Pa). Substantially worse were the results for TAED, which does not disqualify the substance from being used in the bleaching of waste paper pulp, whose composition varies in a wide range

References

Received 04.09.2008 Reviewed 02.10.2008

Figure 8. Comparison of the bleaching effectiveness of dimethylooxsirane (DMD), hydroxy peroxide activated by ammonium molybdate (PaM), cyanamide (PCN) and TAED (PTAED) in the bleaching of waste paper pulp.

Figure 9. Comparison of the two step bleaching effectiveness of dimethylooxsirane (DMD), hydroxy peroxide activated by ammonium molybdate (PaM), cyanamide (PCN) and TAED (PTAED) in the bleaching of waste paper pulp.