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Susceptibility of Deinked Waste Paper Mass to Peroxide Bleaching

Abstract
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. The bleaching of waste paper mass is economically important and technically quite complicated since mechanical pulp of varying compositions are processed. The results presented of trials performed show how the effect of hydrogen peroxide can be enhanced by employing proper activators and other peroxy compounds like peracetic acid in the bleaching of deinked pulp (DIP) from mixed office waste (MOW). The bleaching action of the hydrogen peroxide and other peroxy compounds was intensified under the shield of stabilisers and adequate process conditions preventing excessive decomposition of the peroxide and deterioration of useful properties of the bleached waste paper pulp. The use of hydrogen peroxide and peroxide derivatives in the bleaching of MOW resulted in an effective brightness increase by several percent.

Key words: *waste paper pulp, bleaching peroxide, compound.*

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 peroxy 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 peroxydase. 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.*

Pulp	Kappa number	Brightness, %	Yellowness, %	Ash content, %	Content of metal ions, mg/kg		
					Mn	Fe	Cu
Batch 1	59.9	55.2	10.7	8.90	15.7	37.1	19.6
Batch 2	63.1	61.1	26.1	9.66	15.3	37.7	26.3

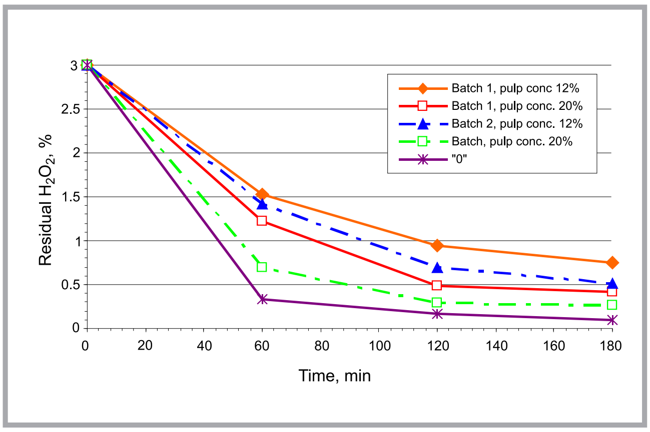

***Figure 1.** Residual H_2O_2 after bleaching at a pulp concentration of 12 and 20% for two waste paper pulp batches with dependence on time; 3% H_2O_2, 0.2% $MgSO_4$, 0.1% EDTA, 0.3% NaOH, pH ≈ 10.5, 90 °C, pulp conc. 12 and 20%.*

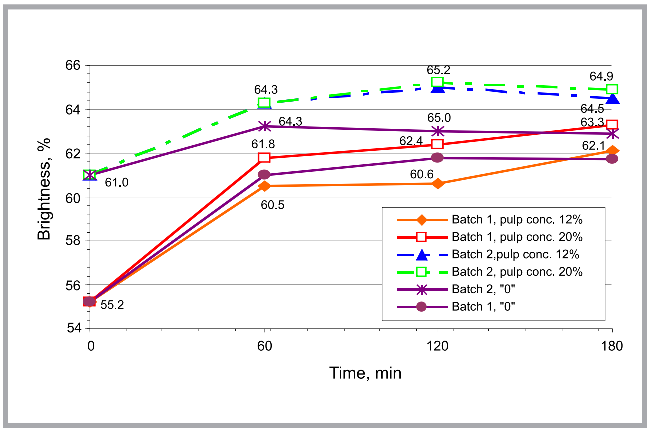

***Figure 2.** Comparison of hydrogen peroxide bleaching effectiveness of waste paper pulp with dependence on bleaching time; 3% H_2O_2, 0.2% $MgSO_4$, 0.1% EDTA, 0.3% NaOH, pH ≈ 10.5, 90 °C, pulp conc. 12 and 20%.*

The elements capable of inhibiting the growth of bacteria, resulting in the too fast decomposition of H_2O_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 peroxide 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 (P) with the addition of its stabilisers: magnesium sulfate ($MgSO_4$) and ethylenediaminetetraacetic acid (EDTA),
- peroxy compounds: peracetic acid (CH_3COOOH), dimethylooxirane (DMD),
- hydroxy peroxide enhanced by the addition of activators: tetraacetylethylendiamine (TAED), cyanamide (NH_2CN) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}$ x $4H_2O$)).

Experimental

Materials

Mixed office waste (MOW) after deinking (initial ink removed) was used in the introductory investigations. The MOW was supplied by International Paper Kwidzyn. The two starting batches of the material are characterised in ***Table 1***.

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 ($MgSO_4$) 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 H_2O_2 was most effectively stabilised by $MgSO_4$,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 efficienter mix of stabilisers is composed of $MgSO_4$ 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 batch1 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

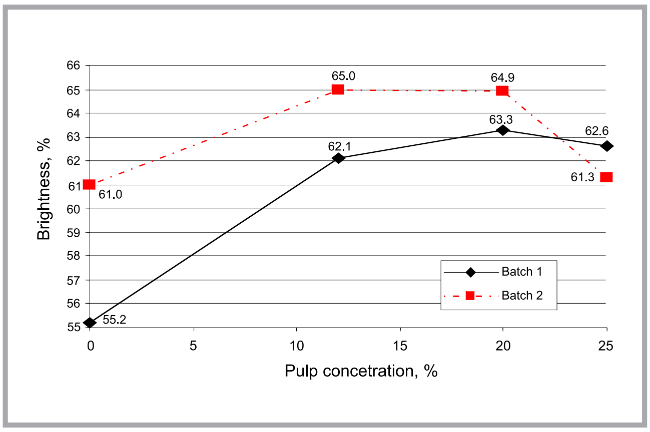

Figure 3. *Comparison of H_2O_2, bleaching effectiveness of waste paper pulp with dependence on pulp concentration; 3% H_2O_2, 0.2% $MgSO_4$, 0.1% EDTA, 0.3% NaOH, pH ≈ 10.5, 90 °C, 180 min.*

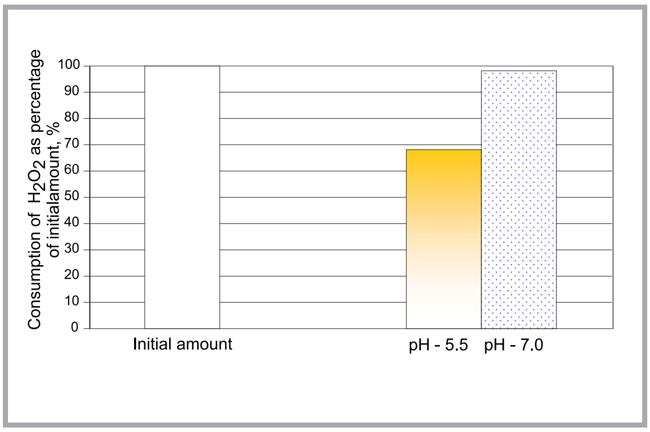

Figure 4. *Exhaustion of hydrogen peroxide after the bleaching of waste paper with peracetic acid with dependence on the reaction medium; (1% Pa as H_2O_2, 0.5% $MgSO_4$, time 60 min, pulp conc. 20%).*

(pH_p ≈ 5.5), at a temperature of 60 °C, (pulp concentration 15%, time 150 min) and 80 °C (pulp concentration - 20%, time - 60 min) produced an improvement in the brightness by 3% on average. The residual amount of hydrogen peroxide and active oxygen was in the range of 5 – 10% of the initial quantity. In bleaching with the same oxidising agents but in neutral medium, practically no residual amounts of H_2O_2 and AO were found (traces) The exhaustive use of the oxidising agents did not positively influence the final pulp brightness, which was 1 – 2% lower in comparison to that after acidic bleaching. (***Figures 4*** and ***5***).

Apart from peracetic acid, pretreatment of the pulp with natrium salts of dicarboxylic acids like EDTA lessens the decomposition of hydroxy peroxide. The pretreatment of the pulp with EDTA (Q – process conducted at 80 °C and pH ≈ 4.5) eased the subsequent bleaching with peracetic acid and hydroxy peroxide since EDTA not only removes iron from the pulp but also inhibits the growth of bacteria, evidenced by an average brightness 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 hydroxy 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-lignifying action of peroxide in the bleaching of waste paper pulp

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

Trial No (Batch 2 pulp)	Pulp conc., %	Time, min	Temp., °C	Pa amount as H_2O_2, %	N_2SiO_3 amount, %	NaOH amount, %	pH_K	Brightness, %
Initial waste paper	---	---	---	---	---	---	---	61.0
67	20	60	80	1.0	---	2.0	4.31	62.0
68	20	60	80	1.0	---	3.0	4.48	63.0
70	20	150	60	1.0	---	3.5	4.62	65.2
71	15	150	60	1.0	---	3.5	4.54	66.8
72	15	150	60	1.0	---	2.0	4.28	66.9
73	15	150	60	1.0	---	1.5	4.17	67.0
88	20	60	80	1.0	0.43	1.5	4.31	61.2
89	20	60	80	0.5	3.0	0.8	5.15	66.0
90*	20	60	80	0.5	0.43	0.8	5.10	66.8

The bleaching of sulfate pulp in neutral medium with peracetic 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 ($NaSiO_3$) (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 H_2O_2.

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%, calulated for an absolute dry pulp. In some of the trials (No. 68, 88, ***Table 2***), a brightness de-

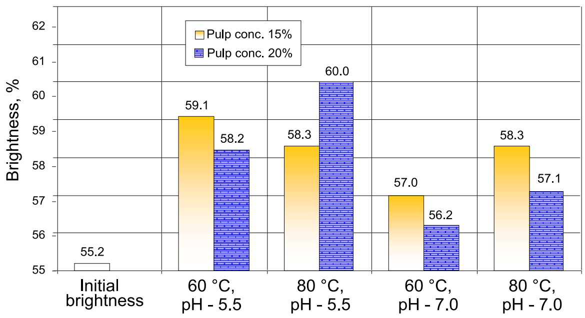

Figure 5.

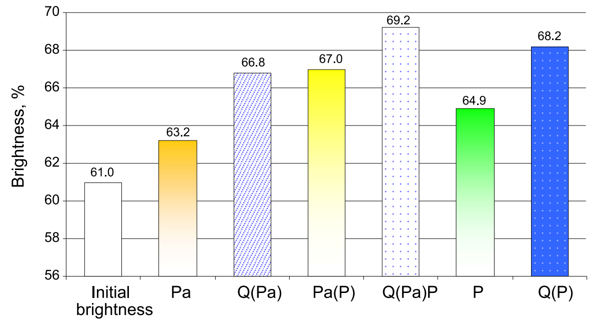

Figure 6.

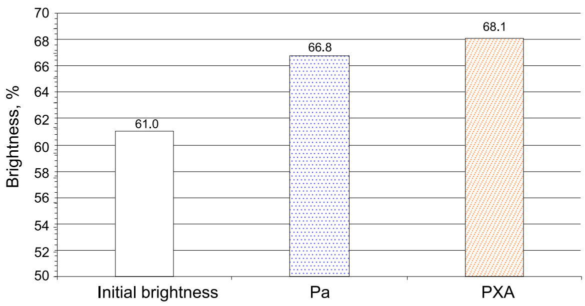

Figure 7.

Figure 5. *Comparison of the bleaching effectiveness of peroxy acetic acid (Pa) on waste paper pulp with dependence on the pH of the bleaching medium; 1% Pa as H_2O_2, 0.5% $MgSO_4$.*

Figure 6. *Comparison of the bleaching action effectiveness of EDTA on the waste paper pulp; Pa-1% Pa as H_2O_2, 0.5% $MgSO_4$, pH - 5.5, time 60 min, pulp conc. 20%; P - 3% H_2O_2, 0.2% $MgSO_4$, 0.1% EDTA, 0.3% NaOH, pH ≈ 10.5, 90 °C, 120 min).*

Figure 7. *Comparison of the bleaching power of peracetic acid (Pa) and mixed peracetic acid (PXA) in the bleaching of waste paper pulp.*

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 3.2) 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 effetive 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_2O_2 to produce a transition form – peroxyimidocarboxylic acid, which is a compound of higher activity than peroxide , and hydrogen peroxide activated by ammonium molybdate - P_{akt} ($(NH_4)_6Mo_7O_{24} \times 4H_2O$), 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 ammoniun 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).

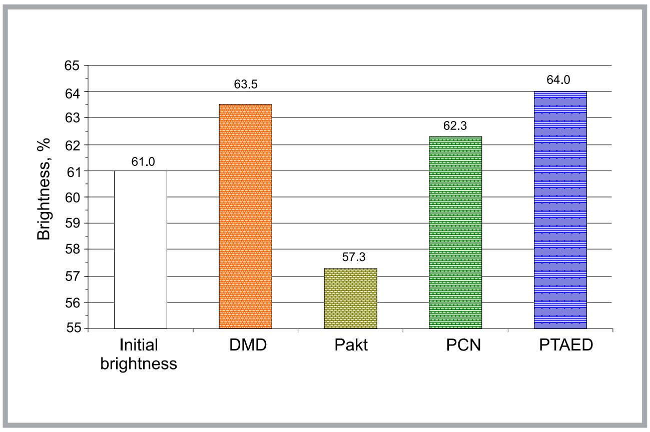

Figure 8. *Comparison of the bleaching effectiveness of dimethylooxsirane (DMD), hydroxy peroxide activated by ammonium molybdate (P_{akt}), cyanamide (P_{CN}) and TAED (P_{TAED}) in the bleaching of waste paper pulp.*

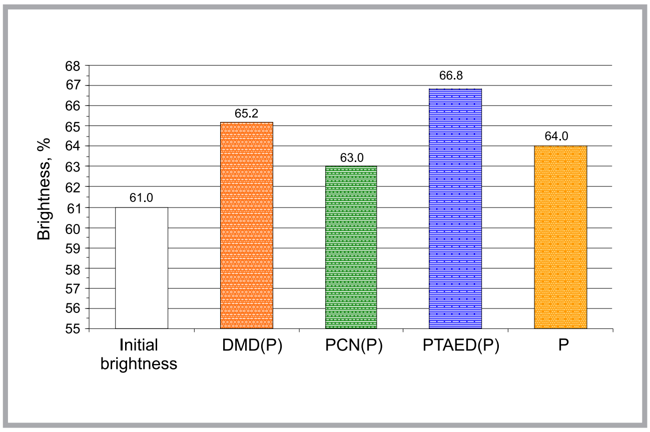

Figure 9. *Comparison of the two step bleaching effectiveness of dimethylooxsirane (DMD), hydroxy peroxide activated by ammonium molybdate (P_{akt}), cyanamide (P_{CN}) and TAED (P_{TAED}) in the bleaching of waste paper pulp.*

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 peroxy 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

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