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Hydrogen Peroxide and Sodium Chlorite ECF Bleaching of Sulphate Hardwood Pulp

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Abstract: The method of hydrogen peroxide and sodium chlorite ECF bleaching of sulphate hardwood pulp has been developed to simplify bleaching due to exclusion of Oxygen-Alkaline bleaching (O) under pressure and industrial production of chlorine dioxide from sodium chlorate. Suggested method consists in hydrogen peroxide delignification of pulp in acidic medium followed by alkaline treatment (instead of EPO) and sodium chlorite bleaching (in acidic medium) by two steps with intermediate oxidative alkaline extraction. Schematically, the process is as following: Pa-E-Ch_1-EP-Ch_2-OxA. The degree of oxidative and hydrolytic degradation of cellulose, the patterns of change in physicochemical, structural and morphological properties of cellulose pulp fibers during the bleaching and the influence of these characteristics on quality of bleached pulp were determined. This testifies to the highly selective delignificating and mild bleaching effect of suggested bleaching scheme on pulp under optimized conditions.

Key words: Hydrogen peroxide · Sodium chlorite · ECF bleaching · Sulphate hardwood pulp

INTRODUCTION

In the present, the pulp and paper industry development is largely depends in increased demand for cost-effective and environmentally friendly techniques of bleaching that requires the extension of study to simplify bleaching technology and reduce the burden on the environment while maintaining the quality of bleached pulp. ECF (Elemental Chlorine Free) bleaching technology satisfies these requirements and suggests the application of oxygen-alkaline treatment (O) at delignification stage and chlorinee dioxide (D) treatment on the stage of repeated bleaching. The advantages of EPO are exclusion of production of harmful chlorine compounds and thus, reduce the burden on wastewater treatment. Oxygen delignification significantly improves the bleaching process and reduces the number of processing steps stipulated by effective pulp washing after EPO [1]. However, the EPO has several disadvantages due to low selectivity and related with the application of structurally complex and expensive equipment, since the process requires the high temperature and high pressure. In addition, a number of studies [1, 2] noted the release of toxic substances in gas emissions using EPO.

In study [3], the evaluation of EPO of eucalyptus pulp with a Kappa number 14-21 showed that in terms of environmental protection, the oxygen delignification is very attractive, but with the economic point of view this process is inefficient.

The treatment of unbleached pulp with hydrogen peroxide after preliminary oxygen catalytic activation [4, 5] attracts the higher interest and can be considered as an alternative to EPO. These works show the study results of acid peroxide bleaching of pulp using peroxide molybdate catalysts: the optimization of eucalyptus pulp bleaching was carried out and the possibility of its use by involvement into industrial bleaching scheme EP-E-O_3-D-P O-A-Z-D-P obtaining EP-P_{Mo}-O_3-D-P O-PMo-Z-D-P; the authors in study [5] have concluded that hydrogen peroxide activated by molybdates can be considered selective bleaching agent, effective for delignification and removal of hexenuronic acids from hardwood pulp.

Molybdenum and its compounds (ammonium molybdate, sodium molybdate, etc.) can be added as a catalyst during pulp treatment by hydrogen peroxide in an acidic medium [4]. It was shown by the example of straw pulp bleaching that addition of phosphomolybdic acid to hydrogen peroxide during acidic preliminary treatment, has increased the whiteness of pulp by 4.8% ISO compared to bleaching without a catalyst [6].

Thus, replacement of the oxygen-alkaline delignification by peroxide in acidic medium is most simple and effective method.

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Pulp bleaching with chlorine dioxide applied in classic technology also has significant disadvantage such as high explosive and, respectively, the inability to transport it, therefore the production of chlorine dioxide is concentrated in the pulp and paper mills.

According to the study results [7], the treatment facilities outside of the plant do not prevent the inflow of waste water containing persistent toxic bioaccumulative and volatile organochlorine compounds from the bleached drainage into nature water reservoir. Only prevention of their production in the bleaching process, i.e. transition to ECF and TCF (Total Chlorine Free) technology ensures the protection of the biosphere from their harmful effect.

The aim of this study was to simplify the technology of sulphate hardwood pulp bleaching and improving its environmental performance, which was solved as following:

- Delignification of pulp by hydrogen peroxide (in acid medium), activated by sodium molybdate (Pa), followed by alkaline treatment, i.e. EPO exclusion from the scheme of sulphate hardwood pulp bleaching;
- Bleaching of pulp (after delignification) by sodium chlorite (Ch) - explosive and water-soluble reagent instead of chlorine dioxide to avoid the special production of chlorine dioxide from production process.

The Main Part: As a result, the proposed scheme for the ECF bleaching is Pa-E-Ch_1-EP-Ch_2, where E and EP are respectively, alkaline and oxidation-alkaline treatment.

Unbleached hardwood pulp (AO "Mondi SLPK") with the degree of penetration 94 PEp.u., Kappa number 20 and breaking length 9520 m was used for bleaching. The system approach applied in the research has included a mathematical modeling, standard and specific assessment techniques used for the industrial control and research practice devoted to pulp and paper production, using modern measurement instruments and computers. Thus, the analysis of experimental data and calculation of optimal parameters of pulp treatment were performed using software package for statistical data analysis Statgraphics Plus ver. 5.0 [8] and L&W FiberTester analyzer to determine the complex of properties of hardwood pulp samples.

The conditions for the Pa and Ch_1 steps have been developed using mathematical experiment planning. Two experiments were planned according to the Box plan (at m = 3) and the effect of bleaching chemicals (H_2O_2 and sodium chlorite), temperature and duration of processes on hardwood pulp were studied. The hardwood pulp yield as well as the degree of penetration at the initial steps and the pulp whiteness in the second experiment has been chosen as the indicators entirely characterizing the delignification and bleaching processes.

Statistical data analysis and process optimization on the steps of Pa and Ch_1 bleaching using a software package Statgraphics Plus ver. 5.0 allowed the formulation of regression equations for the output parameters [9] and the optimal conditions for delignification and bleaching by sodium chlorite (Table 1).

The experimental bleaching carried out in these conditions has corresponded to previously calculated [9].

In order to determine the dynamics of change of physical-chemical and mechanical parameters of hardwood pulp during bleaching, the bleaching was carried out according to full scheme Pa-E-Ch_1-EP-Ch_2-OxA under the following conditions: Pa and Ch_1 stages at developed conditions (Table 1); stage Ch_2 was carried out under the same conditions as the Ch_1 stage with less output of sodium chlorite (1.5% in unit.act.chlorine and 0.5% in unit. ClO_2); AE and EP stages under traditional conditions.

Hardwood pulp bleaching results are shown in Tables 2 and 3 and Figures 1-3.

Table 2 shows that 92% of lignin was removed during pulp bleaching and whiteness reached 88.9 % at low fiber losses.

The decrease of the mechanical strength during bleaching is very moderate (Figure 1). In particular, the breaking length is reduced by 11%, indicating a rather soft conditions of pulp treatment at all stages of bleaching. This is confirmed by the fact that the parameters characterizing the degree of oxidative degradation of hardwood pulp (copper number - estimated content of carbonyl groups in cellulose and solubility in an alkaline solution of sodium zincate - the part of low molecular fractions of cellulose according to Kleinert) are slightly decreased until Pa-E delignification stage and insufficiently changed at further steps.

Table 3 shows the results of the analysis of pulp samples selected after each stage of bleaching using Fiber Tester apparatus. The results shown in the table show that the length of the fibers during bleaching insufficiently changed, the values of structure of fibers are significantly high and slightly varied during bleaching. This parameter correlates with mechanical strength [10], as observed in our experiment.

The swelling and contraction of hardwood pulp fibers depending on the pH of environment during bleaching at different levels are less expressed then for softwood pulp.

Table 1: Optimal conditions of delignification (Pa) and sodium chlorite bleaching (Ch_1)

Number of experiment number - step of process	Reagent consumption, % of abs. dry. fiber	Temperature, °C	Duration, min
# 1 - Pa	H_2O_2 - 3,42	62	118
# 2 - Ch_1	$NaClO_2$ - 3,4-unit.act.chlorine (1,29-unit. ClO_2)	63	148

Table 2: Comparison of unbleached and bleached samples of sulphate hardwood pulp under optimal conditions

	Indices of hardwood pulp				
		Bleached according to scheme			
Hardwood pulp parameters	Initial	Pa-E	Pa-E- Ch_1	Pa-E- Ch_1-EP	Pa-E- Ch_1- Ch_2-Ox
Penetration degree, p.units	94	58	18	11	8
Mass fraction of lignin in pulp, %	3.9	1.7	0.9	0.6	0.3
Yield, % of unbleached hardwood pulp	-	95.2	94.0	93.2	91.7
Chemical pulp copper number, g Cu/100 g	0.17	0.13	0.13	0.13	0.12
Solubility in sodium zincate, %	20.8	19.3	19.6	19.1	18.7
Whiteness, %	45.8	. . .	80.3	82.5	88.9
Whiteness reversion, Pc	-	-	2.33	0.78	1.04

Table 3: Geometric parameters of fiber of sulfate hardwood pulp

	Indices of pulp				
		After bleaching according to schemes			
Hardwood pulp parameters	Initial	Pa-E	Pa-E-Ch_1	Pa-E- Ch_1-EP	Pa-E-Ch_1- Ch_2-Ox
Average length, mm	0.999	0.952	0.960	0.957	0.947
Average width, µm	23.1	22.2	21.8	22.0	21.6
Average form factor, %	93.276	92.308	91.293	91.462	91.185
Callosity, µg/m	108.1	107.7	104.8	105.3	103.4

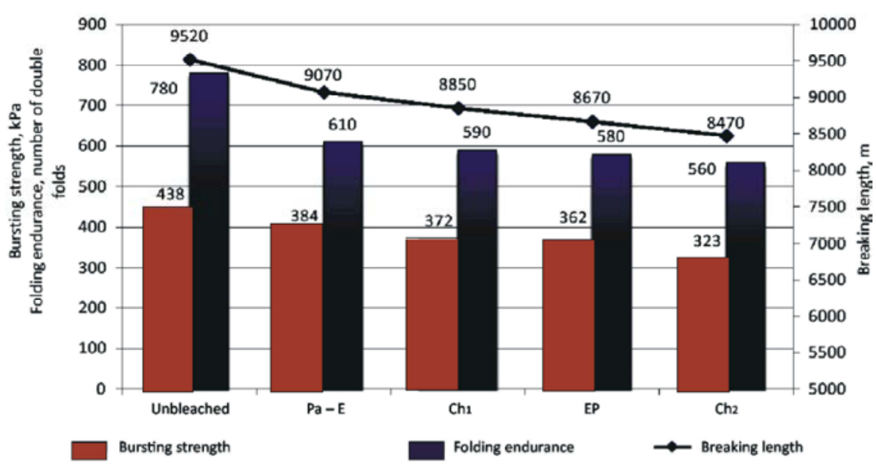

Fig. 1: Changing of strength characteristics of sulphate hardwood pulp during bleaching

In particular, the average values of the fiber width insignificantly decreased after Pa-E stage and maintained unchanged during further bleaching. The changes of fiber coarseness i.e. weight of fiber per fiber length unit were also insufficient. Probably, this is related to the fact that hardwood pulp fibers are narrow with small number of pores therefore there were no significant swelling of fibers observed. Coarseness of fibers slightly reduced only at acid stages of pulp treatment.

The swelling is also related to a decrease in the acidic environment and increase the alkaline levels of water retentivity of hardwood pulp and insignificant change in specific surface of the fibers depending on pH of medium (Figure 2).

Mass fraction of extractive substances and pitch causing "pitch difficulties" in the pulp and paper production is important feature of hardwood pulp. The part of total pitch resin in hardwood sulfate pulp is

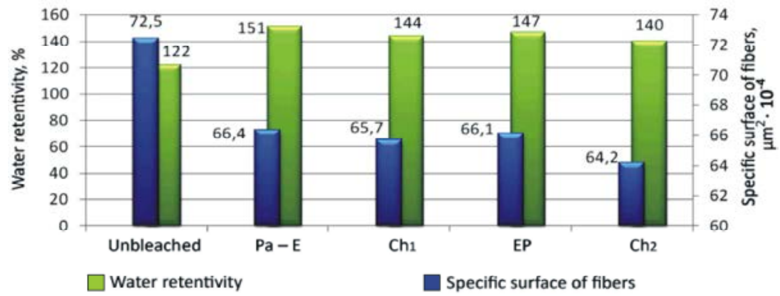

Fig. 2: Changing of water retentivity and specific surface of fibers of sulphate hardwood pulp during bleaching

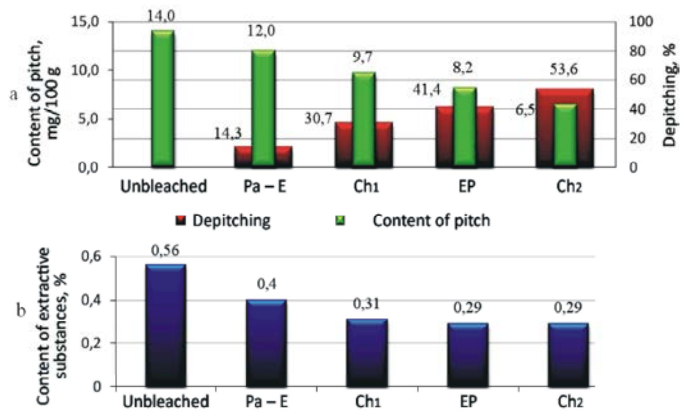

Fig. 3: Mass fraction in sulphate hardwood pulp:
a - pitch; b - extractive substances.

low and is reduced by ~ 50% after bleaching. Whereas the pulp bleaching is carried out using hydrogen peroxide and alkali, the mass fraction of the pitch is 6.5 mg/100 g of bleached pulp (Figure 3).

It is believed that "pitch difficulties" during production process can be avoided at this low value of the pitch.

CONCLUSIONS

The study results have showed that peroxide-alkaline delignification and bleaching by sodium chlorite (instead of chlorine dioxide) is more appropriate for bleaching sulfate hardwood pulp. ECF bleaching of hardwood pulp according to the scheme Pa-E-Ch_1-Ch_2-OxA with a degree of penetration 94 Pep.u. results in pulp whiteness - 88.9% with a very low pitch concentration with insignificant decrease in mechanical strength.

The proposed scheme of hardwood pulp bleaching simplifies the bleaching technology by exclusion of EPO under pressure and avoiding of additional construction of facilities for production of chlorine dioxide using sodium chlorate.

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