(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 101 860 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.05.2001 Bulletin 2001/21

(21) Application number: **00125129.7**

(22) Date of filing: **17.11.2000**

(51) Int Cl.⁷: **D21C 9/10**
// D21C9/153, D21C9/16,
D21C9/14

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **19.11.1999 US 443323**

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(54) Method for bleaching pulp with activated ozone

(57) An ozone based bleaching method for bleaching lignocellulosic materials comprising a bleaching sequence of at least four sequential stages, said stages including an oxidative treatment stage, an alkaline extraction stage, an activated ozone bleaching stage, and a final bleaching stage to produce a pulp of desired final brightness. The activated ozone bleaching stage comprises the addition of an ethanol/DMSO mixture to the pulp prior to the ozone reaction.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] This invention relates to a method for removing lignin from wood pulp, and more particularly to a method for bleaching lignocellulosic materials using activated ozone.

BACKGROUND OF THE INVENTION

[0002] Most pulps obtained from wood pulping processes are dark colored due to the presence of a small fraction of lignin. This residual lignin should be completely removed in the bleaching process to produce a high brightness paper. Until recently, molecular chlorine, sodium hypochlorite and chlorine dioxide were the main reagents used in cellulosic pulp bleaching, in sequences such as C/DEDED, CEHDED, CEHD, CEHDH and CEHED. The pulp quality and the bleaching cost were the main factors that determined the bleaching sequence to be used. However, with the discovery of organochlorinated substances in the effluents, the pulp and paper industry is devoting significant efforts in recent years to search for new technologies that would reduce the discharge of these substances together with the effluents.

[0003] It has been reported that the main source of effluents comes from the cellulosic pulp bleaching process by reaction of molecular chlorine with lignin degradation compounds. See, C. Rappe et al., "On the formation of PCDDs and PCDFs in the bleaching of pulp", Pulp and paper Canada, August, 1989.

[0004] These chlorinated substances are difficult to degrade naturally because they contain carbon-carbon covalent bonds. From among a broad variety of these materials, the substances 2,3,7,8-tetrachloro-dibenzo-furane (TCDF) and 2,3,7,8-tetrachloro-dibenzo-dioxine (TCDD) have shown to be bioaccumulative, potentially toxic and not environmentally sound.

[0005] In response to the pressures resulting from the discovery of these substances in the effluents, the pulp and paper industry is searching for bleaching technologies that allow the production of pulp having good quality while generating an effluent having qualities within the limits imposed by current environmental laws. Thus, bleaching technologies have developed to a point where they are consistently searching for a reduction or elimination of molecular chlorine by the employment of other reagent, such as chlorine dioxide, oxygen, hydrogen peroxide, ozone, enzymes and peracids. The use of these reagents led to the bleaching sequences called ECF (Elemental Chlorine Free) and TCF (Totally Chlorine Free).

[0006] However, such alterations do not seem to be sufficient to meet governmental legislation and public concerns over the environment. Closing the water circuit for the processes used in the pulp and paper industry may soon be a requirement. The employment of ECF and TCF sequences has given the pulp and paper industry the option of closing the water circuit in the bleaching plant through partial or total re-circulation of the effluent to the recovery cycle. Several worldwide kraft pulp concerns are evaluating the closed circuit operation aiming at achieving at reasonable cost the environmental quality and acceptability of their products in the marketplace.

[0007] Attempts have been made to control this problem. It has been known that utilization of oxygen delignification and/or secondary treatment of the effluent were the first measures taken after the detrimental effect of the organochlorinated material on the aquatic organisms was detected. The oxygen delignification stage can remove about 40 to 50% of the residual lignin without significantly affecting the carbohydrates. Therefore, bleaching may be carried out with lower reagent consumption, and consequently a lower discharge of chlorinated organic matter into resulting effluent.

[0008] An important modification in the conventional bleaching sequences is the decrease in molecular chlorine use and the increase in chlorine dioxide consumption. In most pulp mills, replacing molecular chlorine for chlorine dioxide in the first bleaching stage carries out this process modification.

[0009] It has been reported that the AOX (absorbable organic halides) levels in the effluent are significantly reduced by the implementation of oxygen delignification, by the substitution of chlorine by chlorine dioxide, and by the biological treatment of the effluent. Other important environmental pollution indicators, such as color, BOD and COD of the effluent, were also decreased by the utilization of these procedures. See, J.W. Graves et al., "Effect of chlorine dioxide substitution, oxygen delignification and biological treatment on bleach plant effluent", Tappi Journal, July 1993.

[0010] Ozone, a three oxygen based compound, is a strong oxidative agent and highly reactive with lignin. The first kraft pulp treatments were effected in low and high consistencies and it was observed that the ozone dissolution in the fibrous suspension was a determining factor in the process. See, M. Byrd et al.,
"Delignification and bleaching of chemical pulps with ozone: a literature review", Tappi Journal, March 1992.

[0011] Work relating to the use of ozone in ECF and TCF bleaching sequences has been performed by varying reaction consistency employed and the dosage of ozone applied. The ozone stage is preceded by a stage with oxygen, in alkaline medium, and followed by a simple alkaline extraction stage. The final bleaching can be effected by chlorine dioxide (ECF sequences) or hydrogen peroxide (TCF sequences) stages. See, Patent No. WO 91/18145 assigned to B.F. Gregg et al.

[0012] Also, U.S. Patent No. 4,959,124 to Tsai treats softwood kraft pulp with the steps of chlorine dioxide delignification (D), ozone bleaching (Z), alkaline extraction (E, Eo, Ep, Eo) and dissolution.

[0013] Despite advances in the art, there is a need in the industry for a better bleaching technology that is low in operating cost, produces effluent having a lower environmental impact and results in a final product of similar or superior quality.

[0014] Ozone application according to all aforementioned bleaching methods suffers from two major drawbacks. These include: (1) low bleaching efficiency and (2) low bleaching selectivity with regard to pulp lignin. The ozone bleaching efficiency, defined as the units of kappa number dropped across the ozone stage per kilogram of ozone consumed, is usually too low to justify the high ozone bleaching cost. On the other hand, the ozone bleaching selectivity, defined as the ratio of units of kappa number per units of viscosity dropped across the ozone stage, is usually too low, thus impairing pulp quality. Hence, there is a need to find alternative ways to apply ozone in pulp bleaching so that the efficiency and selectivity of the process are improved.

OBJECTS OF THE INVENTION

[0015] It is therefore an object of the invention to providea novel method for pulp bleaching with ozone, such that the overall efficiency and selectivity of the ozone treatment stage is improved. As a consequence, the ozone consumption to reach a target kappa number is lower as compared to conventional ozone bleaching methods. In addition, the final pulp viscosity of the ozone treated pulp obtained with the method of this invention is higher than that achieved with conventional ozone methods.

[0016] It is a further object of the invention to provide a new bleaching process containing an ozone stage which, when compared to conventional pulp bleaching processes, is more efficient and selective, produces an effluent of lower environmental impact, and results in a final product of similar or superior quality.

SUMMARY OF THE INVENTION

[0017] A method for bleaching lignocellulosic materials with activated ozone, comprising a bleach sequence of at least four sequential stages. The sequential stages include an oxidative treatment stage, an alkaline extraction stage, an activated ozone bleaching stage performed in the presence of a mixture of ethanol and dimethyl sulfoxide (DMSO) in appropriate proportions, and a final bleaching stage.

[0018] The oxidative treatment stage may be performed with chlorine, chorine dioxide, ozone, hydrogen peroxide, peracids or any other oxidant, under conditions that are well known to the skilled in the art.

[0019] The alkaline extraction stage may be performed with any source of alkali, preferably sodium hydroxide, under conditions conventionally used in the pulp industry.

[0020] The activated ozone bleaching stage comprises the acidification of the pulp with a mineral acid to render its pH to a value in the range of from about 1.5 to about 5, the treatment of the acidified pulp with an ethanol/DMSO additive mixture, the treatment of the additive treated pulp with ozone, and the subsequent neutralization of the ozone treated pulp with alkali to render the pulp pH to a value in the range of from about 5 to about 10.

[0021] The activated ozone bleaching stage is carried out at a reaction consistency of from about 1% to about 15%, at a reaction temperature of from about 20°C to about 90°C, and at a reaction time of from about 1 to about 120 minutes. The mineral acid dose ranges from about 0.5% to about 4%, the ethanol dose ranges from about 0.001 to about 20%, the DMSO dose ranges from about 0.001 to about 8%, the ozone dosage ranges from about 0.1% to about 1.0% and the alkali dose ranges from about 0.5 to about 3%. All dosages are based on dry pulp fiber weight.

[0022] The activated ozone treated pulp is then washed and/or directly conveyed to the final bleaching operation, wherein it is further treated with chorine dioxide and/or hydrogen peroxide, in one or-more steps, under conditions conventionally known to the skilled in the art, to render a product of desired final quality.

[0023] For purpose of this invention, "kappa number" shall mean the number of milliliters of a 0.1N $KMnO_4$ solution consumed by 1 gram of bone dry pulp and correlates with the pulp bleachability. Viscosity is an indirect measurement of the average degree of polymerization of the pulp cellulose chains and correlates with the pulp strength properties.

[0024] For purpose of this invention, "efficiency" shall mean the number of kappa units (kappa numbers) dropped across the (ZE)-stage per kilogram of ozone applied (kg/t).

[0025] For purpose of this invention, "selectivity" shall mean the percent kappa number divided by the percent viscosity dropped across the (ZE)-stage. The values of pulp kappa number, viscosity and brightness were measured according to Tappi standard procedures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] Other objects, features and advantages will occur to those skilled in the art from the following description of preferred embodiment and the accompanying drawing.

[0027] Figure 1 is a schematic representation of a sequence of bleaching stages that shows the preferred mode of activated ozone application according to the process of this invention.

DETAILED DESCRIPTION OF THE INVENTION

[0028] This invention may be accomplished by pulp treatment with activated ozone after it has been treated with an oxidizing agent and extracted with alkali. After the activated ozone treatment, the pulp is bleached with chlorine dioxide and/or hydrogen peroxide until the desired brightness is achieved.

[0029] Unlike the work performed previously in this area, in the present invention, the ozone stage is activated with a mixture of organic solvents, namely, ethanol and dimethyl sulfoxide (DMSO) in appropriate proportions. The ethanol/ DMSO mixture act synergistically in the ozone stage improving both the efficiency and selectivity of ozone reaction with the pulp.

[0030] The role of the ethanol is to improve the efficiency of ozone bleaching by increasing the rate of lignin removal (kappa units removed/ mass unit of ozone consumed). Ethanol functions as a free radical scavenger during ozone bleaching by capturing certain free radicals, namely hydroxyl and superoxide, which propagates ozone decomposition reactions. By capturing these free radicals, ethanol minimizes ozone losses in undesirable reactions, thus increasing overall process efficiency.

[0031] On the other hand, the role of the DMSO is to improve the selectivity of the ozone stage by decreasing the rate of carbohydrate degradation (viscosity units lost/kappa unit removed). Dimethyl sulfoxide (DMSO) has the property of both functioning as a free radical scavenger and increasing the uniformity of ozone contact with pulp fibers. Consequently, it protects pulp carbohydrates against degradation. DMSO is known to disrupt the ordered water structure by breaking the intra-molecular hydrogen bonds and complexing with water. A change in water structure enhances the diffusion rate of ozone into the water and, consequently, reduces the build up of ozone concentration in localized areas.

[0032] The use of the organic solvent mixture (ethanol/DMSO) in the ozone stage has the unexpected effect of synergistically improving both efficiency and selectivity of the ozone stage at the same time. The organic solvents must be added to the pulp together so that the synergistic effect can be obtained.

[0033] Furthermore, unlike the work performed previously in this area, in the present invention, the treatment with activated ozone is preceded by oxidation and alkali extraction stages, said oxidation and alkali extraction stages being followed by pulp washing. Thus, ozone does not react with previously oxidized lignin compounds that are extracted by the alkali, nor with a pulp having a high kappa number and a high content of transition metals that are partially removed in the oxidation stage.

[0034] In accordance to this invention, the activated ozone reacts more efficiently and selectively with a pulp having a low kappa number that contains a residual lignin low in carry-over material and low in structures containing free phenolic units (or "phenolic lignin"). "Carry-over material" is defined as non-oxidized and oxidized organic matter coming with the pulp from previous stages of the operation. "Phenolic lignin" is defined as that fraction of the lignin incoming with the pulp that contains a free phenolic hydroxyl group. Both carry-over material and phenolic lignin are responsible for the low efficiency and selectivity of the ozone bleaching stage. The low content of carry-over material and the low phenolic character of the pulp treated in accordance with the process of this invention arise from the fact that the pulp is previously treated with an oxidizing agent and alkali in separate stages.

[0035] This invention shows that the activated ozone bleaching stage is most efficient and selective when carried with a pulp that has been previously treated with an oxidizing agent and extracted with alkali.

[0036] This invention relates to a method for bleaching lignocellulosic material from non-wood fibers, hardwoods, softwoods, their mixture, or recycled fibers. The proposed bleaching method is comprised of a number of stages with possible variants in and between the stages. The present invention allows employment from different types of lignocellulosic materials obtained by different types of pulping processes. The lignocellulosic materials may be treated with oxygen prior to the bleaching method of this invention. Oxygen treated lignocellulosic materials are actually preferred in relation to regular ones.

[0037] The first stage of the process involves pulp treatment in an oxidative stage with an oxidant that is aimed at dissolving transition metals, and attacking lignin containing free phenolics units (or phenolic lignin) and carry-over material incoming with the pulp from previous stages.

[0038] The second stage of the process involves pulp treatment in an alkaline extraction stage with any source of alkali. This treatment aims at extracting and solubilizing the compounds oxidized in the previous oxidative stage. It has been suggested that a nucleophilic substitution caused by the alkaline stage is necessary to create new electrophilic attack sites in the remaining lignin structure. See, "The chemistry of delignification". A general concept: Part II", J.

Gierer, January, 1982, *Holzforschung.*

[0039] The third stage of the process, which is the novelty of the present invention, consists of an activated ozone treatment (aZE) of the pulp in acid medium, under conditions that result in maximum decrease of the pulp kappa number with a minimal degradation of its carbohydrates. Among these conditions it is included the addition of a mixture of ethanol/DMSO to the pulp prior to the ozone reaction. The ethanol/DMSO mixture acts synergistically so as to maximize ozone reaction with pulp lignin and minimize ozone reaction with pulp carbohydrates.

[0040] The activated ozone treatment stage is effected at a consistency of from about 1% to about 15% and a temperature of from about 20°C to about 90°C, for reaction periods of from about 1 to about 120 min, with ozone doses of from about 0.1% to about 1.0% based of pulp fiber dry weight. The ethanol/DMSO mixture is added to the pulp immediately before ozone injection. Ideally, the two solvents should be added together as a mixture. The doses of DMSO may vary in the range of from about 0.01% to about 8% based on pulp fiber weight and that of ethanol in the range of from about 0.01% to about 20%. After ozone addition the pulp is neutralized with a suitable alkali source, preferably sodium hydroxide, to a pH in the range of from about 5 to about 10. This neutralization is aimed at destroying the excess acidity and solubilizing the degradation products of ozone reaction with lignin.

[0041] The activated ozone treated pulp is then subsequently bleached with chorine dioxide and/or hydrogen peroxide, to render a product of desired brightness. The process conditions for chorine dioxide and hydrogen peroxide bleaching are well known to those skilled in the art.

[0042] A preferred process of this invention is depicted in Figure 1, which shows the bleaching sequence 10 of DEop (aZE)D. The unbleached pulp 20 is fed into medium consistency pump 30, and is then passed into medium consistency mixer 32 with chlorine dioxide 62 prior to proceeding to D-stage 34. All the pumps and mixers referred to herein are of medium consistency. After treatment and washing in washer 36, the pulp is mixed with sodium hydroxide and hydrogen peroxide 64 prior to pump 38, and is then mixed with oxygen 66 in mixer 40 prior to the Eop extraction stage 42. After washing in washer 44, the pulp is mixed with sulfuric acid 68 and proceeds to pump 46, where it receives the mixture ethanol/DMSO 70, and mixer 48, where the pulp undergoes treatment with ozone 72. The activated ozone treated pulp is then mixed with sodium hydroxide 74 and is transferred to the neutralization tower 52 via pump 50, completing the (aZE)-stage. The pulp is then washed in washer 54 and pumped through pump 56 to mixer 58, where it is treated again with chlorine dioxide 76 in D-stage 60. The resulting bleached pulp 78 is then passed to the final washer.

[0043] The following examples will further clarify the benefits of this invention:

Examples 1-8:

[0044] The pulp employed in this series of examples was obtained from a kraft pulp mill, in the last washing stage after the oxygen delignification, having a kappa number of 9.1, a viscosity of 36.1 mPa.s and a brightness 55% ISO. Example 1 (reference) refers to a pulp treatment with 0.4% ozone based on pulp weight at 10% consistency, 30°C and pH 2.5, followed by alkali neutralization with 1.2% NaOH at 10% consistency, 60°C and 30 min, and pulp washing with excess distilled water. The combination of these chemical treatments is designated from here on as the (ZE)-stage. Example 2 refers to the same treatments described in example 1, except that 10% of ethanol based on fiber weight was added in the ozone stage. Example 3 was effected under the same conditions as example 1, except for the addition of 4% DMSO in the ozone stage. Example 4 was performed similarly to example 1, except for the addition of a mixture of 10% ethanol and 4% DMSO in the ozone stage. Examples 5-8 were done under the same conditions as example 4, except for the dosages of the ethanol/DMSO mixtures, which were varied in a wide range as shown in Table 1. The results of the examples 1 to 8 were interpreted on the basis of (Z_E)-stage efficiency and selectivity and final pulp brightness. The values of pulp kappa number and viscosity measured after the (ZE)-stage were used to calculate the values of efficiency and selectivity.

Table 1.

Performance of the (ZE)-stage carried out with and without additives for hardwood kraft pulp previously delignified with oxygen				
Example #	Additive	Efficiency	Selectivity	Brightness, % ISO
1	No additive (reference)	1.09	1.28	70.8
2	10% EtOH	1.54	1.33	73.0
3	4% DMSO	1.21	1.65	72.1
4	10% EtOH + 4%DMSO	1.71	1.79	74.7

Table 1. (continued)

Performance of the (ZE)-stage carried out with and without additives for hardwood kraft pulp previously delignified with oxygen				
Example #	Additive	Efficiency	Selectivity	Brightness, % ISO
5	7.5% EtOH + 3%DMSO	1.50	1.61	72.6
6	5.0% EtOH + 2%DMSO	1.48	1.53	72.5
7	2.5% EtOH + 1%DMSO	1.37	1.44	72.3
8	1.25% EtOH + 0.5%DMSO	1.23	1.37	71.0

[0045] Comparing examples 1 and 2, it is seen that ethanol addition to the pulp prior to the ozone treatment substantially increases the efficiency of the (ZE)-stage while having only a slight effect on process selectivity. On the other hand, a comparison of examples 1 and 3 indicates that the addition of DMSO prior to the ozone treatment increases (ZE)-stage selectivity substantially while slightly improving efficiency. A comparison of examples 1, 2, 3 with example 4 shows that the efficiency and selectivity gains derived from the addition of the mixture ethanol/DMSO to the pulp prior to the ozone treatment are more than additive. This suggests that these two additives act synergistically to enhance ozone reaction with the pulp. The gain in (ZE)-stage efficiency obtained with the mixture of ethanol/DMSO (57%) is higher than the sum of the gains achieved with ethanol alone (41%) and DMSO alone (11%) which adds up to only 52%. Also, the increase in selectivity derived from the use of the mixture of ethanol/DMSO (40%) is higher than the sum of the selectivity improvements caused by the ethanol (4%) or DMSO (29%) alone, which amounts to 33% only.

[0046] It is obvious from examples 1 to 4 that ethanol is effective to improve the efficiency of ozone reaction with pulp lignin whereas DMSO minimizes ozone attack to pulp carbohydrates, thus increasing selectivity. The combination of these additives in a mixture improves both efficiency and selectivity of ozone bleaching.

Furthermore, when these additives are added as a mixture, their combined effects surmount the sum of each additive individual effect. Hence, it is characterized a synergism between the two additives to improve the efficiency and selectivity of the ozone treatment.

[0047] It should be noted that the synergistic effect appears also when evaluating pulp brightness. The sum of the brightness gains achieved (in relation to the reference) with ethanol alone (2.2% ISO) and DMSO alone (1.3% ISO), which amounts to 3.5% ISO, is lower than the 3.9% brightness gain obtained when these additives are added as a mixture in the ozone treatment.

[0048] Examples 5 to 8 further shows that the (ZE)-stage efficiency, selectivity and brightness improvements derived from pulp treatment with ethanol/DMSO mixture prior to ozone treatment holds true even for additive doses much lower than those described in the example 4. However, the benefits of using the additive mixture tend to decrease as its doses are diminished.

[0049] Bleaching of chemical pulp is usually effected in a sequence of multiple stages. The (ZE)-stage will normally be one of the stages of such a sequence. It is important to determine whether or not the enhanced efficiency, selectivity and brightness gain obtained in the (ZE)-stage, derived from the addition of the DMSO/ethanol mixture to the pulp prior to the ozone reaction, holds true when this stage is applied in a sequence of multiple stages. In other words, it is important to determine the impact of using such additive mixture in the ozone stage on the total bleaching chemical requirement and quality of the finally bleached pulp. This is demonstrated through examples 9 to 13 shown below.

Examples 9 to 13:

[0050] The pulp sample employed in this series of examples was obtained from a kraft pulp mill, in the last washing stage after the oxygen delignification, having a kappa number of 9.1, viscosity 36.1 mPa.s and brightness 55% ISO. The pulp was bleached using five different bleaching protocols.

[0051] Example 9 refers to the DEopDD ECF bleaching sequence that has been used commercially by many pulp mills (reference). The first D-stage was carried out at 10% consistency, 60°C temperature, 30-min reaction and final pH 3.0 (adjusted with sulfuric acid). The Eop-stage was carried with 1.1% NaOH, 0.5% O_2 and 0.5% H_2O_2 based on fiber weight at 10% consistency, 200 kPa pressure, 90°C temperature, 90 min reaction and pH 11.0. The second and third D-stages were carried out at 10% consistency, 70°C temperature, 180-min reaction and final pH 3.8 (adjusted with sodium hydroxide). Pulp washing between stages was effected with excess distilled water. Evaluation of pulp final brightness and viscosity was done according to Tappi standard procedures.

[0052] Example 10 refers to a bleaching sequence using ozone in the first stage of the process, (ZE)DEopD sequence. The (ZE)-stage was performed with 0.4% ozone based on pulp weight at 10% consistency, 30°C and pH 2.5, followed by pulp treatment with 1.2% NaOH at 10% consistency, 60°C and 30 min, and pulp washing with excess distilled water. The first and second D-stages and the Eop-stage were performed under the same conditions and using the same procedures described in example 9.

[0053] Example 11 refers to the same sequence of Example 10, except that the ozone treatment was activated with a mixture of ethanol/DMSO. All bleaching stage conditions were kept the same, except those of the (ZE)-stage where a mixture of 10% ethanol and 4% DMSO was added to the pulp slurry prior to the ozone treatment.

[0054] Example 12 refers to an ECF bleaching sequence using ozone in the third stage of the bleaching process, DEop(ZE)D sequence. This sequence is exactly the same as the one described in example 10, except for the fact that the (ZE)-stage was re-located from the first to the third stage of the sequence. All process conditions and procedures were kept the same as described for example 10.

[0055] Example 13 refers to the same sequence depicted in example 12, except that a mixture of ethanol/DMSO was added to the pulp prior to the ozone treatment. The stage-by-stage conditions used in the various bleaching stages were the same as described for example 12.

Table 2.

Effect of ozone stage activation with a mixture of ethanol/DMSO on overall performance of the sequences (ZE) DEopD and DEop(ZE)D applied to an oxygen delignified hardwood kraft pulp.

Example #	Sequence	Z-stage Additive	Final Bright, ISO	Final Viscosity, mPa.s	ClO_2 Consumption, % on pulp weight				ClO_2/O_3 Replacement Ratio
					Do	D1	D2	Total	
9	DEopDD	-	90.1	15.4	0.692	0.725	0.125	1.542	-
10	(ZE) DEopD	none	90.0	11.8	0.381	0.679	-	1.060	1.20
11	(ZE) DEopD	EtOH/ DMSO	90.2	16.5	0.381	0.419	-	0.800	1.86
12	DEop(ZE) D	none	90.0	13.5	0.381	0.362	-	0.742	2.00
13	DEop(ZE) D	EtOH/ DMSO	90.1	18.1	0.381	0.102	-	0.482	2.65

[0056] A comparison of examples 9 and 10 indicates that ozone application in the first stage of the ECF bleaching process decreases chlorine dioxide requirement in the order of 1.2 kg ClO_2 per kg of ozone applied. However, in this application mode ozone reduces pulp final viscosity (24%) in relation to the reference sequence, without ozone. On the other hand, if ozone is applied in the third stage, the replacement ratio of ozone for chlorine dioxide is substantially increased. A comparison of examples 9 and 12 shows that each kg of ozone applied in the third stage displaces about 2 kg of chlorine dioxide. Furthermore, the viscosity penalty derived from the ozone treatment is much smaller in this case, being the final viscosity value only 12% lower than that of the reference.

[0057] Thus, the proper location of the Z-stage in the bleaching sequence has a significant impact on its efficiency and selectivity.

[0058] Further and significant improvements on ozone stage efficiency and selectivity is achieved through the addition an ethanol/DMSO mixture to the pulp slurry prior to the ozone reaction. This was clearly shown in examples 1 to 8 (Table 1). It is important to note that the benefits derived from the additive mixture are maintained across the bleaching process. A comparison of examples 10 and 11 shows that the additive mixture improved the ClO_2/O_3 replacement ratio from 1.2 to 1.86, i.e., about 55% whereas the final viscosity of the pulp was increased about 28%. This same trend is observed by comparing examples 12 and 13 where the use of the additive mixture resulted in a 33% increase in the ClO_2/O_3 replacement ratio and 34% increase in the final pulp viscosity.

[0059] The final pulp viscosity obtained when the additive mixture was used in the ozone stage (examples 11 and 13) were actually higher than that of the pulp bleached with the reference sequence (example 9). On the other hand, the total amount of chlorine dioxide used in the sequences containing the activated-ozone stage were substantially lower than that of the reference, which makes a good case for the so-called ECF-light bleaching, i.e., ECF bleaching using lower quantities of chlorine dioxide.

[0060] It is obvious from the examples 1 to 13 that the use of ozone according to the process of this invention is much more efficient and selective than with those of conventional ozone bleaching methods. Also, the benefits obtained in the ozone stage (ZE) carries through the overall bleaching sequence. As a result, the total requirement of chlorine dioxide to bleach the pulp is substantially decreased and the pulp final viscosity is significantly increased. By the process of this invention it is understood the addition of an ethanol/DMSO mixture to the pulp prior to the ozone treatment and the location of the ozone treatment in the third stage of the bleaching sequence.

[0061] To further confirm the benefits of the process of this invention, the experimental approach used for examples 1-13 was applied to another type of lignocellulosic material. In the previous examples a hardwood kraft pulp previously delignified with oxygen was used. Examples 14 to 17 were carried out with an oxygen delignified softwood (spruce/pine) kraft pulp, which is more typical of North American pulp mills.

Examples 14 to 17:

[0062] The pulp employed in this series of examples was obtained from a softwood kraft pulp mill, in the last washing stage after the oxygen delignification. The sample had a kappa number of 18.9, viscosity 28.9 mPa.s and brightness of 28.0% ISO. Example 14 (reference) refers to a pulp treatment with 0.3% ozone based on pulp weight at 10% consistency, 30°C and pH 2.5, followed by alkali treatment with 1.2% NaOH at 10% consistency, 60°C and 30 min, and pulp washing with excess distilled water. The combination of these two chemical treatments is designated from here on as the (ZE)-stage. Example 15 refers to the very same treatments expressed in example 14, except that 10% of ethanol based on fiber weight was added to the pulp prior to the ozone treatment. Example 16 was effected under the same conditions as example 14, except for the addition of 4% DMSO to the pulp prior to the ozone reaction. Example 17 was performed similarly to example 14, except for the addition of a mixture of 10% ethanol and 4% DMSO to the pulp prior to the ozone treatment.

[0063] The results of the examples 14-17 were interpreted on the basis of (ZE)-stage efficiency and selectivity and final pulp brightness. The values of kappa number and viscosity measured after the (ZE)-stage were used to calculate the values of efficiency and selectivity.

Table 3.

Performance of the (ZE)-stage carried out with and without additives for softwood kraft pulp previously delignified with oxygen

Example #	Additive	Efficiency	Selectivity	Brightness, ISO
14	No additive (reference)	1.15	1.27	37.7
15	10% EtOH	1.55	1.29	40.1
16	4% DMSO	1.20	1.65	38.2
17	10% EtOH + 4%DMSO	1.73	1.81	41.5

[0064] A comparison between examples 14 and 15 indicates that addition of ethanol to the ozone treatment substantially increases the efficiency of the (ZE)-stage while having only a slight effect on process selectivity. On the other hand, a comparison between examples 14 and 16 shows that the addition of DMSO to the pulp prior to the ozone treatment increases (ZE)-stage selectivity substantially while slightly improving efficiency. A comparison of examples 14, 15 and 16 with example 17 shows that the benefits of the ethanol and DMSO addition to the ozone stage are more than additive, suggesting that these additives act synergistically to improve ozone bleaching performance. The increase in (ZE)-stage efficiency obtained with the mixture of ethanol plus DMSO (50.4%) is higher than the sum of the gains achieved with ethanol alone (34.8%) and DMSO alone (4.3%), which adds up to 39% only. Also, the increase in selectivity derived from the use of the mixture of Ethanol/DMSO (42.5%) is higher than the sum of the selectivity improvements caused by the ethanol (1.6%) or DMSO (30%) alone, which amounts to 31.6% only.

[0065] It is obvious from examples 14-17 that ethanol is effective to improve the efficiency of the (ZE)-stage whereas DMSO enhances (ZE)-stage selectivity. The combination of these additives in a mixture improves both efficiency and selectivity of the (ZE)-stage.

Furthermore, when the additives are added together, the gains derived from each individual additive is surmounted by the sum of their individual gains. Hence, it characterizes a synergistic effect between the two additives to improve the efficiency and selectivity of the ozone treatment.

[0066] It should be noted that the synergistic effect appears also when evaluating pulp brightness. The sum of the brightness gains achieved with ethanol alone (2.4% ISO) and DMSO alone (0.5% ISO) which amounts to 2.9% ISO is lower than the 3.8% brightness gain obtained when these additives are added as a mixture in the ozone treatment.

[0067] The benefits of adding the ethanol/DMSO mixture in the ozone stage of multiple-stage ECF bleaching sequences is shown in the examples 18 to 22. The benefits of such a treatment are quantified by its impact of final pulp viscosity and total chlorine dioxide requirement to reach a target brightness of 90% ISO.

Examples 18 to 22:

[0068] The softwood pulp (spruce/pine) sample employed in this series of examples was obtained from a kraft pulp mill, in the last washing stage after the oxygen delignification. The pulp had a kappa number of 18.9, viscosity of 28.9 mPa.s and brightness of 28.0% ISO. The pulp was bleached using five bleaching protocols.

[0069] Example 18 refers to the DEopDD ECF bleaching sequence that has been used commercially by many pulp mills. The first D-stage was carried out at 10% consistency, 60°C temperature, 30-min reaction and final pH 3.0 (adjusted with sulfuric acid). The Eop-stage was carried with 1.1% NaOH, 0.5% 02 and 0.5% H202 based on fiber weight at 10% consistency, 200 kPa pressure, 90°C temperature, 90 min reaction and pH 11.0. The second and third D-stages were carried out at 10% consistency, 70°C temperature, 180-min reaction and final pH 3.8 (adjusted with sodium hydroxide). Pulp washing between stages was effected with excess distilled water. Evaluation of pulp final brightness and viscosity was done according to Tappi standard procedures.

[0070] Example 19 refers to a bleaching sequence using ozone in the first stage of the process, (ZE)DEopD sequence. The (ZE)-stage was performed with 0.3% ozone based on pulp dry weight at 10% consistency, 30°C and pH 2.5, followed by alkali treatment with 1.2% NaOH at 10% consistency, 60°C and 30 min, and pulp washing with excess distilled water. The first and second D-stages and the Eop-stage were performed under the same conditions and procedures as described for example 18.

[0071] Example 20 refers to the same sequence of example 19, except for the fact that a mixture of 10% ethanol and 4% DMSO was added to the pulp slurry prior to the ozone treatment. All other bleaching conditions were kept the same as described in example 19.

[0072] Example 21 refers to an ECF bleaching sequence using ozone in the third stage of the bleaching process, DEop(ZE)D sequence. This sequence is exactly the same as the one described in example 19, except that the ozone treatment was re-located from the first to the third stage of the sequence. All process conditions and procedures were kept the same as described for example 19.

[0073] Example 22 refers to the same sequence depicted in Example 21, except that a mixture of 10% ethanol and 4% DMSO was added to the pulp slurry prior to the ozone treatment. The stage-by-stage conditions used in this sequence were the same as in example 21.

Table 3.

Effect of ozone stage activation with a mixture of ethanol/DMSO on overall performance of the sequences (ZE) DEopD and DEop(ZE)D for an oxygen delignified softwood kraft pulp.

Example #	Sequence	Z-stage Additive	Final Bright, ISO	Final Viscosity, mPa.s	ClO_2 Consumption, % on pulp weight				ClO_2/O_3 Replacement Ratio
					Do	D1	D2	Total	
18	DeopDD	-	90.0	19.9	1.725	0.764	0.191	2.680	-
19	(ZE) DeopD	none	90.1	14.3	1.006	1.114	-	2.120	1.87
20	(ZE) DeopD	EtOH/ DMSO	90.1	18.5	1.006	0.909	-	1.915	2.55
21	DEop(ZE) D	none	90.1	18.8	1.006	0.884	-	1.890	2.63
22	DEop(ZE) D	EtOH/ DMSO	90.0	23.9	1.006	0.651	-	1.657	3.41

[0074] A comparison of examples 18 and 19 indicates that ozone application in the first stage of the ECF bleaching sequence, for the softwood pulp, decreases chlorine dioxide requirement in the order of 1.87 kg ClO_2 per kg of ozone applied. However, in this application mode ozone causes a penalty on pulp viscosity of about 28%, in relation to the reference sequence without ozone. On the other hand, if ozone is applied in the third stage the replacement ratio of ozone for chlorine dioxide is substantially increased. A comparison of examples 18 and 21 shows that each kg of ozone applied in the third stage displaces about 2.63 kg of chlorine dioxide.
Furthermore, the viscosity penalty derived from ozone application in the third stage is much smaller, being only 5%

lower than that of the reference.

[0075] Thus, the results for the softwood kraft pulp sample also indicate that proper location of the Z-stage in the bleaching sequence has a significant impact on overall efficiency and selectivity of the bleaching process.

[0076] Significant improvements on ozone stage efficiency and selectivity can also be achieved through the addition of a mixture of ethanol/DMSO to the softwood pulp slurry, prior to the ozone reaction. This was clearly shown in examples 14 to 17. What is important to note is that these benefits are maintained across the bleaching process. A comparison between examples 19 and 20 shows that the use of such additive mixture improved in 36% the ClO_2/O_3 replacement ratio, from 1.87 to 2.55, whereas the final viscosity of the pulp was increased about 29%. This same trend is observed by comparing examples 21 and 22 where the use of the additive mixture resulted in a 30% increase in the ClO_2/O_3 replacement ratio and 27% increase in the final pulp viscosity. The final pulp viscosity obtained when the additive mixture was added to the pulp prior to the ozone treatment (example 22) was actually higher than that of the pulp bleached with the reference sequence without ozone (example 18).

Furthermore, the total amount of chlorine dioxide used in the sequences containing the activated ozone stage was substantially lower than that of the reference.

[0077] Specific features of the invention, particularly as provided in Figure 1, are for convenience only, as each feature may be combined with other features in accordance with the invention. Alternative embodiments will be recognized by those skilled in the art and are intended to be included within the scope of the claims.

Claims

1. A method for bleaching lignocellulosic materials comprising the sequential steps of:

    a) treating pulp in an oxidative stage with an oxidizing agent to dissolve transition metals, and oxidizing lignin containing phenolic lignin and carry-over material incoming with the lignocellulosic pulp;
    b) extracting said pulp through an alkaline extraction treatment stage to extract and solubilize said pulp from step (a) ;
    c) treating said pulp from step (b) through an activated ozone treatment stage with activated ozone to oxidize lignin and other colored materials remaining in the pulp, said activated ozone treatment stage comprises adding pulp slurry of a mineral acid, a mixture of ethanol/DMSO, and a gas stream containing ozone, followed by pulp neutralization with alkali; and d) treating the pulp from step (c) through one or more bleaching stages with a bleach selected from the group consisting of hydrogen peroxide and chlorine dioxide.

2. The method of claim 1 wherein said step for treating pulp with activated ozone in step (c) comprises sequentially adding mineral acid, a mixture of ehtanol/DMSO, an ozone gas stream, and an alkali to neutralize any excess acid and extract the ozone-oxidized lignin from the pulp.

3. The method of claim 2 wherein said treating with an activated ozone in step (c) comprises adding mineral acid having a dosage sufficient to render the pulp to a pH to a value in the range of 1.5-5.

4. The method of claim 2 wherein said treatment with an activated ozone comprises adding a mixture of ethanol/DMSO to the pulp having a dose of about 0.01% to about 20% ethanol and from about 0.01% to about 8% DMSO based on pulp fiber dry weight.

5. The method of claim 4 wherein said ethanol/DMSO mixture is comprised of about 5% to about 10% ethanol and from about 2% to about 4% DMSO, based on pulp fiber dry weight.

6. The method of claim 4 wherein said ethanol/DMSO mixture is prepared prior to being added to the pulp slurry.

7. The method of claim 2 wherein said step for treating with the activated ozone comprises addition of ozone gas to the pulp having a dosage of from about 0.1% to about 1.0%, based on pulp fiber dry weight.

8. The method of claim 7 wherein said step for treating with activated ozone comprises the addition of ozone gas to the pulp having a dosage preferably of from about 0.3% to about 0.6%, based on pulp fiber dry weight.

9. The method of claim 2 wherein said step for treating with activated ozone comprises adding alkali to the ozone treated pulp at a dose sufficient to neturalize the pulp pH to a range of from about 5 to about 10.

10. The method of claim 1 wherein said step for treatment under activated ozone comprises carrying out a reaction consistency of from about 1% to about 15%, a reaction temperture of from about 20°C to about 90°C, and a reaction time of from about 1 minute to about 120 minutes.

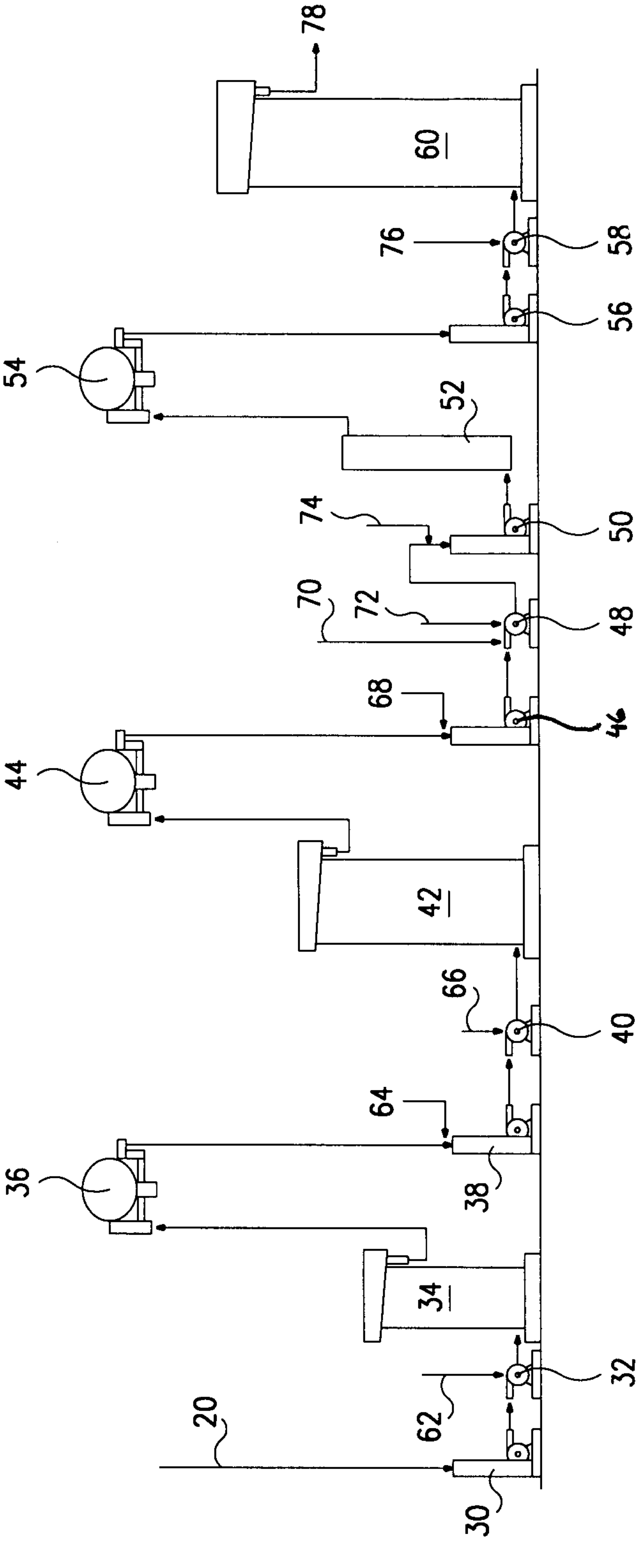
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FIG. I

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EUROPEAN SEARCH REPORT

Application Number
EP 00 12 5129

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	25 January 2001	Karlsson, L

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Application Number
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