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(54) Method for applying ozone in ECF bleaching

(57) An ECF bleaching method for bleaching lignocellulosic materials (20) comprising a bleaching sequence of at least three sequential stages, said stages including an oxidative treatment stage (34), an alkaline extraction stage (42), and an acidification bleaching treatment stage (48) using ozone (70).

A preferred process is shown in Fig. 4, which shows the bleaching sequence (10) of DEo(ZE)D.

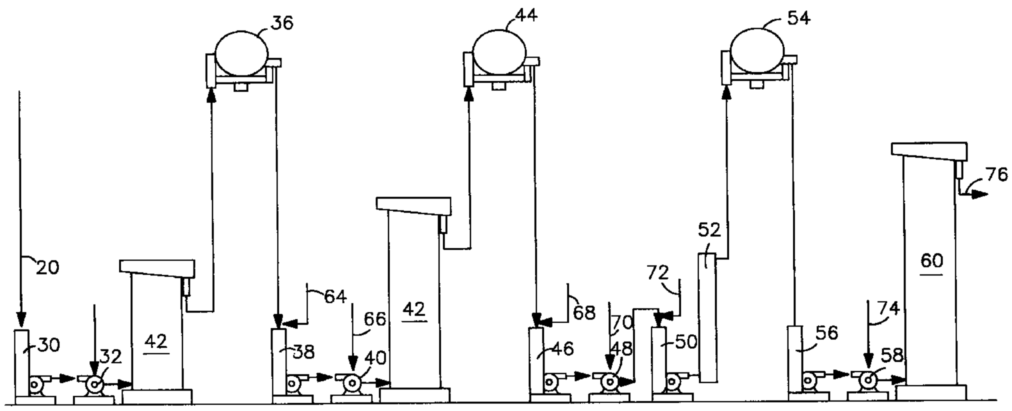

FIG. 4

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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 ozone.

BACKGROUND OF THE INVENTION

[0002] Most of the 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 the 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 which determined the bleaching sequence to be used. However, with the discovery of organochlorinated substances in the effluents, the pulp and paper industry is spending significant efforts in the recent years searching for new technologies which 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 are comprised of carbon-carbon covalent bonds. From among a broad variety of these materials, the substances 2,3,7,8-tetrachlorodibenzofurane (TCDF) and 2,3,7,8-tetrachlorodibenzodioxine (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, pre-bleaching, bleaching and post-bleaching technologies have arisen. The new bleaching technologies have consistently searched for a reduction or elimination of molecular chlorine by the employment of other reagents, such as chlorine dioxide, oxygen, hydrogen peroxide, ozone, enzymes and organic 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 recirculation of the effluent to the recovery cycle. Several worldwide kraft pulp industries 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 of the mills, this change in the operation is effected by replacing the molecular chlorine with chlorine dioxide in the first bleaching stage.

[0009] It has been reported that the AOX (adsorbable 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. It is first use as a bleaching agent for fibrous substances, including those used for the manufacture of paper, wherein the fibers are subjected to a chlorine dioxide and ozone gas mixtures. The first kraft pulp ozonolysis 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 the ozone stage in its location in the sequence, in the reaction consistency employed and in the dosage of ozone applied.

For example, ozone has been shown to be useful in the bleaching sequence. The ozone stage is preceded by a stage with oxygen, in alkaline medium, and followed by a simple alkaline extraction stage, or else the extraction supplied with oxygen, with peroxide or with oxygen and hydrogen peroxide. The final bleaching can be effected by chlorine dioxide (ECF sequences) or hydrogen peroxide (TCF sequences) stages. See, Patent No. WO 91/18145 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) and alkaline extraction (E, Eo, Ep, Eo).

[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.

OBJECTS OF THE INVENTION

[0014] It is therefore an object of the invention to provide a new bleaching technology through an ECF bleaching sequence with ozone, such that a lower consumption of chemicals is required, especially of ozone and chlorine dioxide, for bleaching pulp to a similar level of brightness, than the conventional pulp bleaching process.

[0015] It is a further object to provide for a new bleaching technology through an ECF bleaching sequence with ozone which, when compared to the conventional pulp bleaching processes, is lower in operational cost, produces an effluent of lower environmental impact, and results in a final product of similar or superior quality.

SUMMARY OF THE INVENTION

[0016] This invention is directed to a ECF bleaching method for bleaching lignocellulosic materials comprising a bleaching sequence of at least three sequential stages, the stages including an oxidative treatment stage, an alkaline extraction stage, and an acidification bleaching treatment stage using ozone.

[0017] The oxidative treatment stage comprises a chlorine dioxide treatment employing a kappa factor between 0.05 and 0.40, with a pH of between from about 2 to about 5, at a reaction consistency in the range of from about 3% to about 15%, a reaction temperature of between about 20°C to about 90°C, and a reaction time of from about 10 minutes to about 180 minutes.

[0018] In one embodiment, the alkaline extraction stage comprises an addition of an alkali source to render the pH of the reaction to above about pH 10, at a reaction time of from about 30 minutes to about 180 minutes, a reaction consistency range of from about 5% to about 15%, and a reaction temperature of from about 50°C to about 120°C.

[0019] The alkaline extraction stage comprises a treatment with oxygen having a dosage of from about 0.2% to about 1.2%, at a reaction pressure of from about 100 kPa to about 500 kPa. The alkaline extraction stage also includes a treatment with peroxide having a dosage of from about 0.2% to about 1.5%. The alkaline extraction stage further comprises addition of a magnesium having a dosage of from about 0.01% to about 0.2%.

[0020] The acidification bleaching stage comprises a treatment at a pH of from about pH 0 to about pH 5 using a mineral acid, the treatment having a reaction consistency of from 1% to about 15%, at a reaction temperature of from about 20°C to about 90°C, and a reaction time of from about 1 minute to about 60 minutes. The ozone dosage ranges from about 0.1% to about 1.0% on a dry pulp basis. The acidification bleaching treatment stage is followed by an alkaline treatment comprising an addition of an alkali source to render the pH of the reaction to about 11.0, the reaction time of from about 5 minutes to about 90 minutes, and the reaction temperature of from about 40°C to about 90°C. The acidification bleaching treatment stage is followed by an alkaline treatment. The alkaline treatment step may be preceded by an intermediate washing.

[0021] The acidification bleaching treatment stage further comprises addition of chlorine dioxide at a dosage of from about 0.1% to 3.0% on a dried pulp basis to achieve a desired brightness at a final pH of from about pH 2 to about pH 5.5, with a reaction consistency in the range of from about 1% to about 15%, at a reaction time of from about 30 minutes to about 300 minutes, in a reaction temperature of from about 30°C to about 90°C.

[0022] Two separate chlorine dioxide stages may be added. A washing stage may take place between the chlorine dioxide stages. An alkaline extraction stage may take place between the separate second chlorine dioxide extraction stages. In a further embodiment, one or two hydrogen peroxide stages may be added instead of the final one or two chlorine dioxide stages. The hydrogen peroxide in a dosage of from about 0.5% to about 3.0% on a dried pulp basis to achieve a desired brightness at a final pH in the range of from about pH 9.0 to about pH 12.0, with a reaction consistency of from about 5% to about 25%, at a reaction time of from about 30 minutes to about 240 minutes, and in a reaction temperature of from about 30°C to about 120°C. The addition of a magnesium having a dosage of from about 0.02% to about 0.2%, on a dry pulp basis.

[0023] This invention is also directed to a ECF bleaching method for bleaching lignocellulosic materials comprising a bleaching sequence which includes a plurality of stages in sequential order, the stages including an oxidative treatment stage, an alkaline extraction stage and an acidification bleaching treatment stage using ozone.

[0024] The acidification bleaching treatment stage comprises an addition of ozone in a pulp ozonolysis step, at a reaction pH of from about pH 0 to about pH 5, a reaction consistency range of from about 0.1% to about 1.0% on a dry pulp basis, and a reaction temperature of from about 20°C to about 60°C.

[0025] Moreover, this invention is directed to a bleaching method for ECF bleaching of lignocellulosic material comprising a bleaching sequence, the method comprising delignifying the lignocellulosic material using oxygen to form a delignified pulp; bleaching the delignified pulp with chlorine dioxide forming a bleached pulp; extracting the bleached pulp using an alkali source forming an alkaline extracted pulp; treating the alkaline extracted pulp with ozone in an acidic medium forming an ozone treated pulp; treating the ozone treated pulp with an alkali source; and bleaching the ozone treated pulp. Another embodiment accounts for an intermediate washing prior to treating the ozone treated pulp with an alkali source.

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 embodiments and the accompanying drawings, in which:

Fig. 1 is a bar graph representing the variation of bleaching efficiency at the different sequences shown in Tables I, II and III. The bleaching efficiency was obtained by means of a ratio between the total variation of the brightness and the total charge of oxidative reagents (chlorine dioxide, oxygen, ozone and hydrogen peroxide), expressed as "OXE" (Oxidative Equivalents);

Fig. 2 is a bar graph similar to Fig 1, representing the variation of bleaching efficiency at different sequences shown in Tables I and II;

Fig. 3 is a bar graph showing the variation of the bleaching efficiency for several bleaching sequences shown in Tables III and IV using the process of this invention; and

Fig. 4 is a schematic representation of this sequence of one embodiment of this invention.

DETAILED DESCRIPTION OF THE INVENTION

[0027] This invention may be accomplished by pulp treatment with ozone after it has been oxidized with chlorine dioxide and extracted with alkali. After the ozone treatment, the pulp is extracted again with alkali and then bleached with chlorine dioxide until the desired brightness is achieved.

[0028] Unlike the work performed previously in this area, in the present invention, treatment with ozone is preceded by a chlorine dioxide and an alkali extraction step. Thus, ozone does not react with previously oxidized lignin compounds which are extracted by the alkali, nor with a pulp having a high kappa number. In accordance to the claimed invention, the ozone reacts more selectively with a pulp having a low kappa number which contains a residual lignin low in free phenolic structures. These structures are responsible for the low selectivity of the ozone bleaching, and the low phenolic character of the pulp arises from a previous treatment with chlorine dioxide followed by alkaline extraction.

[0029] This invention shows that ozone bleaching is most efficient when carried out after the pulp has been oxidized with chlorine dioxide and extracted with alkali. Moreover, the present invention contains an alkaline extraction step between the chlorine dioxide and the ozone stages. Thus, ozone would not have to react with chlorine dioxide degraded compounds and would more effectively react with a pre-bleached pulp having a low kappa number.

[0030] This invention relates to an ECF method for bleaching lignocellulosic material from hardwoods, softwoods, their mixture, or recycled fibers. The proposed bleaching method is comprised of a number of steps, with possible variants in and between the steps. The present invention allows employment of different types of lignocellulosic materials obtained by different types of pulping processes. The lignocellulosic material may optionally be treated with oxygen prior to the bleaching method of this invention.

[0031] The first step, which is optional, consists of a pulp delignification treatment with oxygen aiming at the maximum reduction in the residual lignin content without significantly impairing the cellulose chain degree of polymerization. This treatment can vary from a simple and conventional oxygen stage to the utilization of double stages, also including the addition of chelation agents and hydrogen peroxide. To better understand this step, a more detailed description is described below:

- Process (O) is a conventional delignification with oxygen which comprises an oxygen pressurized treatment of the brown pulp in alkaline medium, at low, medium or high consistency;
- Process (OO) is a double stage oxygen delignification, wherein the brown pulp is pressurized in the oxygen treatment in alkaline medium in two stages without washing between them;
- Process OQ(OP) is a double stage oxygen delignification, wherein the brown pulp is first pressurized in an oxygen treatment in alkaline medium, at a medium consistency. Then the pulp is washed, treated with chelation agents

(e.g., EDTA and DTPA), and washed again. A second oxygen pressurized stage in alkaline medium is then employed, and the hydrogen peroxide in this stage may also be used.

[0032] The differences among these three oxygen delignification systems are efficiency and selectivity. The last process system described results in the greatest efficiency and selectivity although it has the highest operational and installation costs. It is important that the pulp goes to the bleaching plant with the lowest possible kappa number so as to have the lowest reagent consumption.

[0033] During the oxygen delignification step, the decrease of the kappa number of the pulp varies from about 40-50% for the systems (OO) and OQ(OP)

[0034] The second step of the process involves pulp treatment with chlorine dioxide at a medium consistency and in acid medium (pH<4). The amount of chlorine dioxide used in this process can be expressed by an index here named as kappa factor, which relates the kappa number of the unbleached pulp with the percent of active chlorine used in the referred stage. For the present invention this kappa factor can vary from 0.05 to 0.40, which will depend on the type of wood employed in the process for obtaining the pulp, the type of pulp, how and if the oxygen delignification was effected and the availability of chlorine dioxide. This stage is represented usually in the industry by the symbol "D_0" or "D_{100}".

[0035] This step can also employ molecular chlorine and chlorine dioxide mixtures, the combination being more effective for pulp delignification than chlorine or chlorine dioxide alone. These mixtures can be effected in the forms: (DC), (CD) and (C+D).

[0036] The brightness achieved in this stage varies from 60 to 75% ISO, for kappa factors varying from 0.10 to 0.24, respectively. In case of a casual change for a TCF sequence, the first chlorine dioxide stage can be replaced by a simple acidification or else by a chelation stage.

[0037] The third step includes an alkaline extraction stage (E) aiming at solubilizing the compounds oxidized in the chlorine dioxide 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*. This alkaline extraction stage can be proceeded with oxygen (Eo), hydrogen peroxide (Ep), or a combination thereof (Eop). A fourth variant of the alkaline extraction is the pressurized processes, (PO), Pp or P_{HT}, wherein elevated temperatures and greater dosages of oxygen and peroxide in relation to the Eop stage are generally used.

[0038] In this third step, the kappa number varies from 2.0 to 7.0, the brightness from 70 to 80% ISO and the viscosity from 18 to 35 cP.

[0039] A fourth step of the present invention consists of an ozone treatment of the pulp in acid medium, under conditions that result in maximum decrease of the kappa number with a minimal degradation of the carbohydrates. Among these conditions is the utilization of chlorine dioxide together with ozone, wherein a probable synergistic effect may occur due to the simultaneous action of both reagents. Other conditions of optimization is the use of chelation agents for the control of metal profile, control of pH, pulp consistency, control of ozone concentration and gas/pulp contact efficiency. Before the ozone treatment, a chelation agent, for example oxalic acid, diethylenetetraamine pentaacetic acid (DTPA) or diethylenetriamine tetraacetic acid (EDTA), may be applied to the pulp to reduce the content of metals comprised therein.

[0040] After the treatment with the chelation agent, the pH of the pulp is preferably adjusted to a range between 0 and 5 before the application of ozone. The consistency in which the ozone stage is carried out may be high, medium or low. High consistency is advantageous since it provides an efficient gas/pulp contact surface, in view of the fact that the pulp floccus are "fluffed" before the ozone delignification stage. The drainage/pressing of the pulp to obtain the high consistency is considered to be a washing step, wherein the dissolved organic material may be recycled to the mill recovering plant.

[0041] As a fifth step, the pulp obtained after the ozone stage may or may not be subjected to a rapid alkaline extraction to solubilize the compounds degraded during the reaction of lignin with ozone. This pulp has a kappa number of less than 4.0, a brightness between 80-86% ISO and a viscosity between 13-25 cP. This alkaline extraction can be effected with oxygen (Eo), peroxide (Ep) or oxygen plus peroxide [Eop, (PO), Pp or P_{HT}].

[0042] The sixth step and beyond are bleaching stages involving chlorine dioxide and/or hydrogen peroxide to achieve final brightness and viscosity of 86-90% ISO and 12-25 cP, respectively.

[0043] A preferred process of this invention is shown in Fig. 4, which shows the bleaching sequence 10 of DEo(ZE)D. Pulp 20 from the post oxygen washer 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/or hydrogen peroxide) 64 prior to pump 38, and is then mixed with oxygen 66 in mixer 40 prior to the Eo (or Eop) extraction stage 42. After washing in washer 44, the pulp is mixed with sulfuric acid 68 and proceeds to pump 46 and mixer 48, where the pulp undergoes treatment with ozone 70. The ozone treated pulp is then mixed with sodium hydroxide 72 and is transferred to extraction stage 52 via pump 50. The pulp is then washed in washer 54 and pumped through pump 56 to mixer 58, where it is treated again with chlorine dioxide 74 in D-stage 60. The resulting bleached pulp 76 is then passed to the final washer.

EXAMPLES 1-7

[0044] The pulp employed in this series of examples was obtained in a laboratory through the ITC (IsoThermal Cooking) process having a 17.3 kappa number, a 39.3% ISO brightness and a 78.2 cP viscosity. The conditions employed in the bleaching steps for this series of examples are the following:

(OO)-Stage: the oxygen delignification was conducted in a 600 kPa pressurized reactor for 90 minutes at 95°C. Dosages of 1.8% sodium hydroxide, 1.8% oxygen and 0.3% magnesium sulfate on a dry basis were applied to the pulp at a consistency of 12%;
D_0-Stage: chlorine dioxide was mixed with the pulp at a consistency of 12%, this stage being conducted in polyethylene bags in a water bath at 70°C for 30 minutes;
Eo and Eop-Stages: the pulp at a consistency of 12% was subjected to an oxidative alkaline extraction with oxygen in a pressurized reactor at the temperature of 90°C and a reaction time of 15 minutes under 200 kPa pressure, and of 75 minutes at atmospheric pressure. A charge of 0.5% magnesium sulfate was added, and unless otherwise mentioned, the charge of hydrogen peroxide used was 0.5%;
Z-stage: the ozone stage was carried out in the previously acidified pulp at a consistency of 45%, room temperature and a time of about 30 seconds. The pulp sample was acidified at a pH of 2.5 with 4N sulfuric acid, at a consistency of 6%, maintained at room temperature for 5 minutes and then drained off to a consistency of about 37%. The pulp was then fluffed and the consistency again determined, varying from between 40-45%. Immediately after the ozonolysis was carried out with 25 g of oven dry equivalent pulp, in a glass reactor fitted to a rotary evaporator;
(ZD)-stage: the pulp was treated in this step in the same way as described for the Z-stage, the dilution of the pulp with water and chlorine dioxide to a consistency of 12% being carried out immediately after this stage. This chlorine dioxide stage was carried out in polyethylene bags in a water bath at 70°C for 30 minutes;
(ZE)-Stage: after the ozonolysis the pulp was immediately treated with a sodium hydroxide solution at a pH of about 11.0, temperature of 70°C and reaction time of 30 minutes;
D-stage: the chlorine dioxide stage was conducted at 70°C and at a consistency of 12% for 180 minutes;
Washing: the pulp was washed between each stage with an excess of distilled water either in a box containing a screen or in a buchner funnel. No washing was effected between stages (OO), (ZD) and (ZE).

[0045] A first comparison of the process of this invention with those from the art is shown in Table I. This table shows the results of final brightness and viscosity of the pulp, total dosage of chlorine dioxide, saving of chlorine dioxide in kg per kg of O_3 used and bleaching efficiency.

[0046] Upon evaluating examples 1, 2 and 3, it is observed no significant chlorine dioxide savings due to the use of ozone in the bleaching process. However, the use of the process of this invention, example 4, resulted in a reduction of about 57% in the total consumption of chlorine dioxide, with a saving of 1.95 kg of ClO_2 per kg of O_3 used. This significant reduction in the consumption of dioxide has a very positive impact in the closing of the bleaching plant circuit. Further, the pulp bleached by this process showed high final brightness and viscosity. On the other hand, the bleaching efficiency of this process was superior to the conventional bleaching process.

[0047] It is observed that the increase in the ozone charge (example 5) or the utilization of hydrogen peroxide in the alkaline extraction (examples 6 and 7) is efficient in relation to examples 2 and 3. These alterations resulted in significant reductions in chlorine consumption of 42%, 20% and 47%, respectively. However, when compared with the sequence of this invention, DEo(ZE)D (example 4), the sequence presented lower efficiency and selectivity, showed by the lesser chlorine dioxide saving and the lesser final viscosity values to achieve the same brightness level.

[0048] Upon analyzing the bleaching efficiency values of the process in the art, it is verified that the use of a greater ozone charge (examples 2 vs. 5) results in a slight increase of this parameter, while the utilization of hydrogen peroxide was detrimental (examples 2 vs. 6).

[0049] The process of this invention presented the greatest bleaching efficiency value (2.30%) among the sequences Z-ECF evaluated, being 26.4% and 16.8%, which are superior to the ones of examples 5 and 7, respectively. Here, an increase in the bleaching efficiency means that in order to achieve a similar final brightness a lower consumption of oxidative reagents occurred in the process of this invention in relation as compared to the conventional processes.

TABLE I

Example	Bleaching Sequence	Chemical Charge Applied (kg/odt of pulp)						Total ClO_2, kg/odt	ClO_2 Savings[2]	Bright, % ISO	Visc, cP	Bleach, Effic[3] %
1	(OO)[1]DEoDD	D	Eo		D		D	13.7	-	90.1	30.5	2.18
		ClO_2	NaOH	O_2	ClO_2		ClO_2					
		9.6	5.2	6	3.0		1.1					
2	(OO)ZEoDD	Z	Eo		D		D	12.2	0.38	89.3	17.2	1.75
		O_3	NaOH	O_2	ClO_2		ClO_2					
		4	8.8	6	4.6		7.6					
3	(OO)(ZD)EoDD	(Z	D)	Eo		D	D	13.7	0	90.5	21.4	1.72
		O_3	ClO_2	NaOH	O_2	ClO_2	ClO_2					
		4	6.1	6.1	6	6.1	7.6					
4	(OO)DEo(ZE)D	D	Eo		(Z	E)	D	5.9	1.95	90.4	23.4	2.30
		ClO_2	NaOH	O_2	O_3	NaOH	ClO_2					
		4.4	5.2	6	4	7.8	1.5					
5	(OO)ZEoDD	Z	Eo		D		D	8	0.95	89.7	13.1	1.82
		O_3	NaOH	O_2	ClO_2		ClO_2					
		6	8.8	6	5.7		2.3					
6	(OO)ZEopDD	Z	Eop			D	D	11	0.68	90	15.1	1.71
		O_3	NaOH	O_2	H_2O_2	ClO_2	ClO_2					
		4	12.9	6	3	7.6	3.4					
7	(OO)(ZD)EopD	(Z	D)	Eop			D	7.2	1.62	90.2	19.5	1.97
		O_3	ClO_2	NaOH	O_2	H_2O_2	ClO_2					
		4	6.1	11.2	6	3	1.1					

[1] Double stage oxygen delignified pulp: 10.6 kappa, 51.6% ISO brightness and 44.8 cp viscosity.
[2] Chlorine dioxide savings (kg ClO_2/kg O_3).
[3] Bleaching Efficiency: calculated by the ratio between Brightness Gain throughout the sequence and Oxidation Equivalents (OXE) consumed in the sequence

EXAMPLES 8-11

[0050] The pulp employed in this series of examples was obtained in laboratory through the ITC process, having a 13.1 kappa number, a 45.4% ISO brightness and a 52.5 cP viscosity. The conditions employed in the bleaching steps for this series of examples were the same as the previous series (examples 1 to 7), except by the pre-delignification stage with oxygen, which is described below:

[OQ(Op)]-stage: delignification with oxygen was conducted in a reactor for 30 minutes at 95°C. Dosages of 1.6% sodium hydroxide and of 0.3% magnesium sulfate were applied over the pulp at a consistency of 12%, and the pressure of the system was maintained at 600 kPa with oxygen. After delignification with oxygen, the pulp was washed exhaustively with distilled water and then subjected to a stage with 0.1% of DTPA for 5 minutes at 90°C and with a consistency of 5%. Again the pulp was exhaustively washed with distilled water, and then subjected to a new delignification with oxygen, in a reactor for 60 minutes at 95°C. Dosages of 0.3% magnesium sulfate, 1% of sodium hydroxide and 0.5% of hydrogen peroxide were applied over the pulp at a consistency of 12% and the system was pressurized to 600 kPa with oxygen.

[0051] Table II describes the results of final brightness and viscosity of the bleached pulp, total dosage of chlorine dioxide, saving of chlorine dioxide and bleaching efficiency for the process of this invention and the conventional processes. Example 11 clearly shows greater efficiency as compared with the conventional process, with a saving of 1.20 kg of ClO_2 per kg of O_3 consumed. On the contrary, the conventional as shown in examples 9 and 10 provides value for efficiency of 0.78 and 0.90, respectively. As shown by these examples, the process sequence results in similar final brightness, consumes less ozone and/or chlorine dioxide as well as providing a high final viscosity in relation to the conventional process sequences.

[0052] In this series of examples, the process sequence showed the greatest bleaching efficiency among the sequences Z-ECF. With an increase of about 8.5% in relation to example 10, the sequence of this invention, DEop(ZE)D, showed to be more efficient in the utilization of the oxidative reagents. Note that example 8 is employed only as a reference since ozone is not used. It is important to emphasize that the use of the process of this invention resulted in an extremely low chlorine dioxide consumption in the entire process and this represents a great advantage from the viewpoint of closing the bleaching plant.

TABLE II

Example	Bleaching Sequence	Chemical Charge Applied (kg/odt of pulp)							Total ClO_2, kg/odt	ClO_2 Savings[2]	Bright, % ISO	Visc, cP	Bleach, Effic[3] %
		D	Eop					D					
8	OQ(Op)[1]DEopD	ClO_2	NaOH	O_2	H_2O_2			ClO_2	7.7	-	90.9	22.4	1.41
		7.3	10	6	3			0.4					
		Z	Eop					D					
9	OQ(Op)ZEopD	O_3	NaOH	O_2	H_2O_2			ClO_2	3.8	0.78	90.2	11.5	1.04
		5	18.7	6	5			3.8					
		(Z	D)	Eop				D					
10	OQ(Op)(ZD)EopD	O_3	ClO_2	NaOH	O_2	H_2O_2		ClO_2	4.1	0.90	90.2	14.9	1.18
		4	3	10	6	3		1.1					
		D	Eop			(Z	E)	D					
11	OQ(Op)DEop(ZE)D	ClO_2	NaOH	O_2	H_2O_2	O_3	NaOH	ClO_2	4.1	1.20	90.3	19.0	1.28
		3	10	6	3	3	6	1.1					

[1] Double stage oxygen delignified pulp: 80 kappa, 69.8% ISO brightness and 29.1 cp viscosity.
[2] Chlorine dioxide savings (kg ClO_2/kg O_3).
[3] Bleaching Efficiency: calculated by the ratio between Brightness Gain throughout the sequence and Oxidation Equivalents (OXE) consumed in the sequence

EXAMPLES 12-16

[0053] The pulp employed in this series of examples was obtained after a conventional delignification stage with oxygen on industrial scale, having a 9.5 kappa number, a 54.0% ISO brightness and a 26.5 cP viscosity. The conditions used in the bleaching steps were similar to the previous series of examples, the only differences in the stages being described below:

D1-stage: chlorine dioxide was mixed with the pulp at a consistency of 10%, this stage being conducted in polyethylene bags in a vapor bath at 60°C for 30 minutes;
Eop-stage: the pulp at a consistency of 10% was subjected to oxidative alkaline extraction with oxygen in a pressurized reactor at 200 kPa, a temperature of 95°C and a reaction time of 90 minutes. A charge of 0.5% magnesium sulfate was added;
(ZD)-stage: the pulp was treated in this step in the same way as described in the "Z-stage", however, the dilution was carried out to a consistency of 10%. The chlorine dioxide stage was effected in polyethylene bags in a vapor bath at 60°C for 30 minutes;
(DZ)-stage: the acidification described in item "Z-stage" was replaced here by the chlorine dioxide which was carried out at a pH between about 2.5 to about 3.0, at 60°C for 30 minutes. Then the pulp was drained off and, thereafter treated with ozone;
(ZE)-stage: the reaction time for this stage was 15 minutes;
D-stage: the treatment was conducted at 70°C, consistency of 10%, for 180 minutes;
Washing: the pulp was washed between each stage with an excess of distilled water either in a box containing a screen of 120 mesh or in a buchner funnel. No washing was effected between stages (ZD), (DZ) and (ZE).

[0054] Table III shows the results comparing the sequence of the present study with those of the art by treating an industrial kraft-O pulp. They show once more that the sequence DEop(ZE)D (example 16) is more efficient in the use of the oxidative reagents with reasonable values of bleaching efficiency, final brightness and viscosity.

[0055] The process of this invention required 59% less chlorine dioxide in relation to the reference sequence (example 12) resulting in a saving of 1.40 kg of chlorine dioxide/kg of O_3 consumed. The conventional sequence (example 13) showed lower efficiency with a reduction of about 37% in the chlorine dioxide consumption.

[0056] The bleaching efficiency for the sequence of the present study was superior (2.3%) to the conventional sequences of examples 14 and 15, which are also considered to be efficient sequences.

TABLE III

Example	Bleaching Sequence	Chemical Charge Applied (kg/odt of pulp)								Total ClO_2, kg/odt	ClO_2 Savings[2]	Bright, % ISO	Visc, cP	Bleach Effic[3] %
12	O[1]DEopDED	D	Eop			D		E	D	12.1	-	89.8	15.6	1.84
		ClO_2	NaOH	O_2	H_2O_2	ClO_2		NaOH	ClO_2					
		8.7	12	6	5	3		3	0.4					
13	OZEopDED	Z	Eop			D		E	D	7.6	0.90	90.1	12.0	1.62
		O_3	NaOH	O_2	H_2O_2	ClO_2		NaOH	ClO_2					
		5	18	6	5	5.7		3	1.9					
14	O(ZD)EopDED	(Z	D)	Eop			D	E	D	6.4	0.86	90.7	13.0	1.71
		O_3	ClO_2	NaOH	O_2	H_2O_2	ClO_2	NaOH	ClO_2					
		5	4.3	12	6	5	1.9	3	0.2					
15	O(DZ)EopDED	(D	Z)	Eop			D	E	D	6.4	0.86	90.3	8.6	1.69
		ClO_2	O_3	NaOH	O_2	H_2O_2	ClO_2	NaOH	ClO_2					
		4.3	5	12	6	5	1.9	3	0.2					
16	ODEop(ZE)D	D	Eop			(Z	E)	D		5.1	1.40	89.8	12.7	1.75
		ClO_2	NaOH	O_2	H_2O_2	O3	NaOH	ClO_2						
		4.3	12	6	5	5	6.5	0.8						

[1] Double stage oxygen delignified pulp: 9.50 kappa, 54.0% ISO brightness and 26.5 cp viscosity.
[2] Chlorine dioxide savings (kg ClO_2/kg O_3).
[3] Bleaching Efficiency: calculated by the ratio between Brightness Gain throughout the sequence and
5 Oxidation Equivalents (OXE) consumed in the sequence

EXAMPLES 17-23

[0057] The pulp employed in this series of examples was obtained after a conventional delignification stage with oxygen on industrial scale and presented a 10.6 kappa number, a 45.8% IS0 brightness and a 27.2 cP viscosity at the beginning of the experimentation.

[0058] The main difference in the procedure of this series of examples was the utilization of the pressurized peroxide (PO) bleaching instead of a simple oxidative alkaline extraction supplied with oxygen and peroxide, prior to the Z-stage. The pulp treatment with pressurized peroxide was effected in a reactor at a consistency of 10%, pressure of 600 kPa with oxygen, temperature of 95°C and a reaction time of 120 minutes. The charges used in the pulp were: 0.8% of hydrogen peroxide, 0.5% of O_2, 1.6% of sodium hydroxide and 0.5% of magnesium sulfate.

[0059] Table IV shows how the industrial kraft-O pulp behaved in view of the different Z-ECF sequences. It can be noted that the ozone stage is at several positions in the sequences, wherein the two variants of the present invention (examples 20-23) showed the greatest final brightness. The low viscosity presented by example 20 was improved when a rapid and simple alkaline extraction was effected, immediately after the ozone stage (example 21).

[0060] A comparison of examples 22 and 23 shows that the pressurized peroxide stage is a good substitute for the alkaline extraction supplied with oxygen and hydrogen peroxide. The examples shows the efficiency in the reduction of ozone charge applied to achieve the same brightness and a slightly superior viscosity.

[0061] The sequence of the present invention as illustrated by examples 21 and 22 showed the highest values for bleaching efficiency. The use of ozone in the sequence of example 22 led to an increase of 22.9% in comparison with example 19 of the conventional sequence.

[0062] The intensification of the alkaline extraction showed in example 23 lowered the bleaching efficiency of the process of this invention. The reason for this was the employment of high dosages of hydrogen peroxide and oxygen which did not have a significant effect on the reduction of the chlorine dioxide and ozone consumption.

TABLE IV

Example	Bleaching Sequence	Chemical Charge Applied (kg/odt of pulp)							Total ClO_2, kg/odt	Bright, % ISO	Visc. cP	Bleach, Effic[3], %
17	O[1]ZEopD	Z	Eop			D			10	85.5	12.8	1.79
		O_3	NaOH	O_2	H_2O_2	ClO_2						
		5.9	15	4	4	10						
18	OZEop(ZD)	Z	Eop			(Z	D)		10	79.7	13.9	1.59
		O_3	NaOH	O_2	H_2O_2	O_3	ClO_2					
		3.1	15	4	4	2.1	10					
19	O(ZD)EopD	(Z	D)	Eop			D		14	86.6	13.8	1.79
		O_3	ClO_2	NaOH	O_2	H_2O_2	ClO_2					
		4	4	15	4	4	10					
20	ODEopZD	D	Eop			Z	D		14	88.2	7.6	1.74
		ClO_2	NaOH	O_2	H_2O_2	ClO_2	ClO_2					
		4	15	4	4	5.3	10					
21	ODEop(ZE)D	D	Eop			(Z	E)	D	14	89.9	11.5	1.81
		ClO_2	NaOH	O_2	H_2O_2	O_3	NaOH	ClO_2				
		4	15	4	4	5.3	7.4	10				
22	ODEop(ZE)D	D	Eop			(Z	E)	D	10	87.1	12.7	2.20
		ClO_2	NaOH	O_2	H_2O_2	O_3	NaOH	ClO_2				
		4	15	4	4	3.2	7.4	6				
23	OD(PO)(ZE)D	D	(PO)			(Z	E)	D	10	87.1	13.9	1.71
		ClO_2	NaOH	O_2	H_2O_2	O_3	NaOH	ClO_2				
		4	16	8	8	1.6	7.4	6				

[1] Double stage oxygen delignified pulp: 10.6 kappa, 45.8% ISO brightness and 27.2 cp viscosity.
[2] Chlorine dioxide savings (kg ClO_2/kg O_3).
[3] Bleaching Efficiency: calculated by the ratio between Brightness Gain throughout the sequence and Oxidation Equivalents (OXE) consumed in the sequence.

[0063] Specific features of the invention are shown in one or more of the drawings 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 ECF bleaching method for bleaching lignocellulosic materials comprising a bleaching sequence of at least three sequential stages, said stages including an oxidative treatment stage, an alkaline extraction stage, and an acidification bleaching treatment stage using ozone.

2. The bleaching method of claim 1 wherein said oxidative treatment stage comprises a chlorine dioxide treatment employing a kappa factor between 0.05 and 0.40, with a pH of between from about 2 to about 5, at a reaction consistency in the range of from about 3% to about 15%, a reaction temperature of between about 20°C to about 90°C, and a reaction time of from about 10 minutes to about 180 minutes.

3. The bleaching method of claim 1 wherein said alkaline extraction stage comprises an addition of an alkali source to render the pH of the reaction to above about pH 10, at a reaction time of from about 30 minutes to about 180 minutes, a reaction consistency range of from about 5% to about 15%, and a reaction temperature of from about 50°C to about 120°C.

4. The bleaching method of claim 1 wherein said acidification bleaching stage comprises a treatment at a pH of from about pH 0 to about pH 5 using a mineral acid, the treatment having a reaction consistency of from 1% to about 15%, at a reaction temperature of from about 20°C to about 90°C, and a reaction time of from about 1 minute to about 60 minutes.

5. The bleaching method of claim 1 wherein said acidification bleaching treatment stage comprises an addition of ozone in a pulp ozonolysis step, at a reaction pH of from about pH 0 to about pH 5, a reaction consistency range of from about 1% to about 50%, an ozone dosage range of from 0.1% to about 1.0% on a dry pulp basis, and a reaction temperature of from about 20°C to about 60°C.

6. The bleaching method of claim 1 wherein said acidification bleaching treatment stage is followed by an alkaline treatment comprising an addition of an alkali source to render the pH of the reaction to about 11.0, the reaction time of from about 5 minutes to about 90 minutes, and the reaction temperature of from about 40°C to about 90°C.

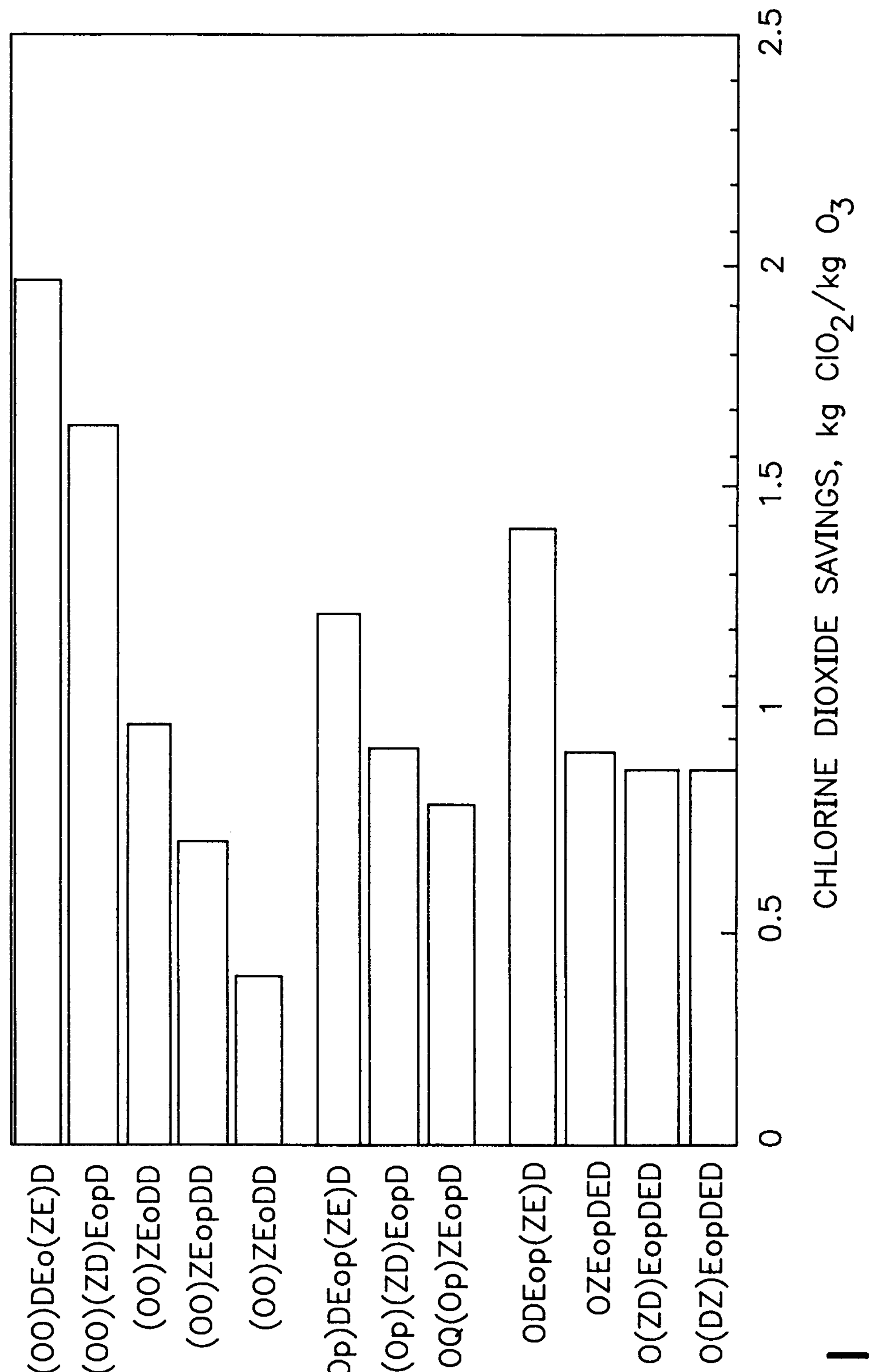
7. The bleaching method of claim 1 wherein said acidification bleaching treatment stage is followed by an alkaline treatment.

8. A ECF bleaching method for bleaching lignocellulosic materials comprising a bleaching sequence which includes a plurality of stages in sequential order, said stages including an oxidative treatment stage, an alkaline extraction stage and an acidification bleaching treatment stage using ozone.

9. The bleaching method of claim 8 wherein said acidification bleaching treatment stage comprises an addition of ozone in a pulp ozonolysis step, at a reaction pH of from about pH 0 to about pH 5, a reaction consistency range of from about 1.0% to about 50% on a dry pulp basis, and a reaction temperature of from about 20°C to about 60°C.

10. A bleaching method for ECF bleaching of lignocellulosic material comprising a bleaching sequence, said method comprising

    a) delignifying said lignocellulosic material using oxygen to form a delignified pulp;
    b) bleaching said delignified pulp with chlorine dioxide forming a bleached pulp;
    c) extracting said bleached pulp using an alkali source forming an alkaline extracted pulp;
    d) treating said alkaline extracted pulp with ozone in an acidic medium forming an ozone treated pulp;
    e) treating said ozone treated pulp with an alkali source; and
    f) bleaching said ozone treated pulp.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1.5
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2.5
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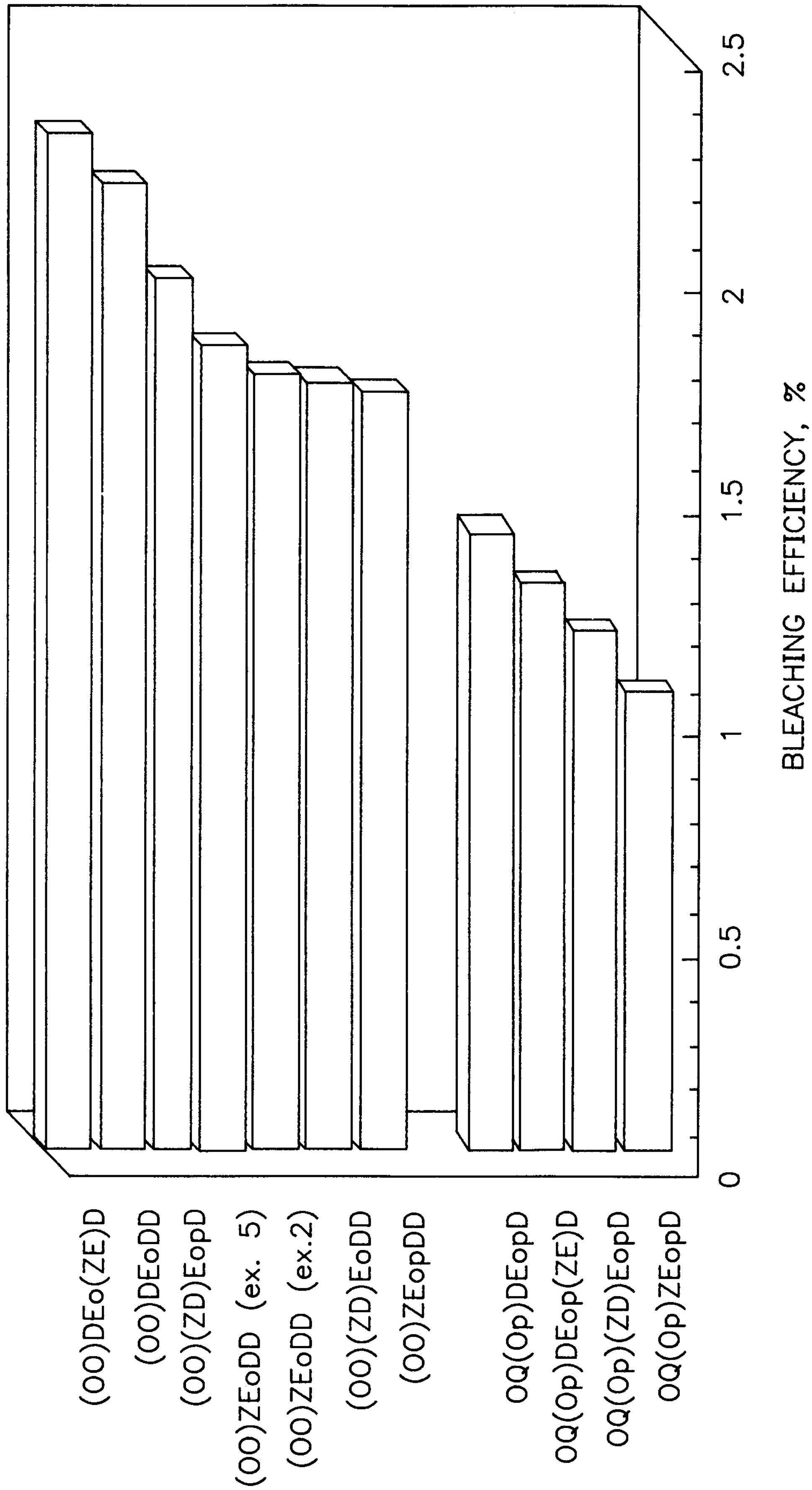
FIG. I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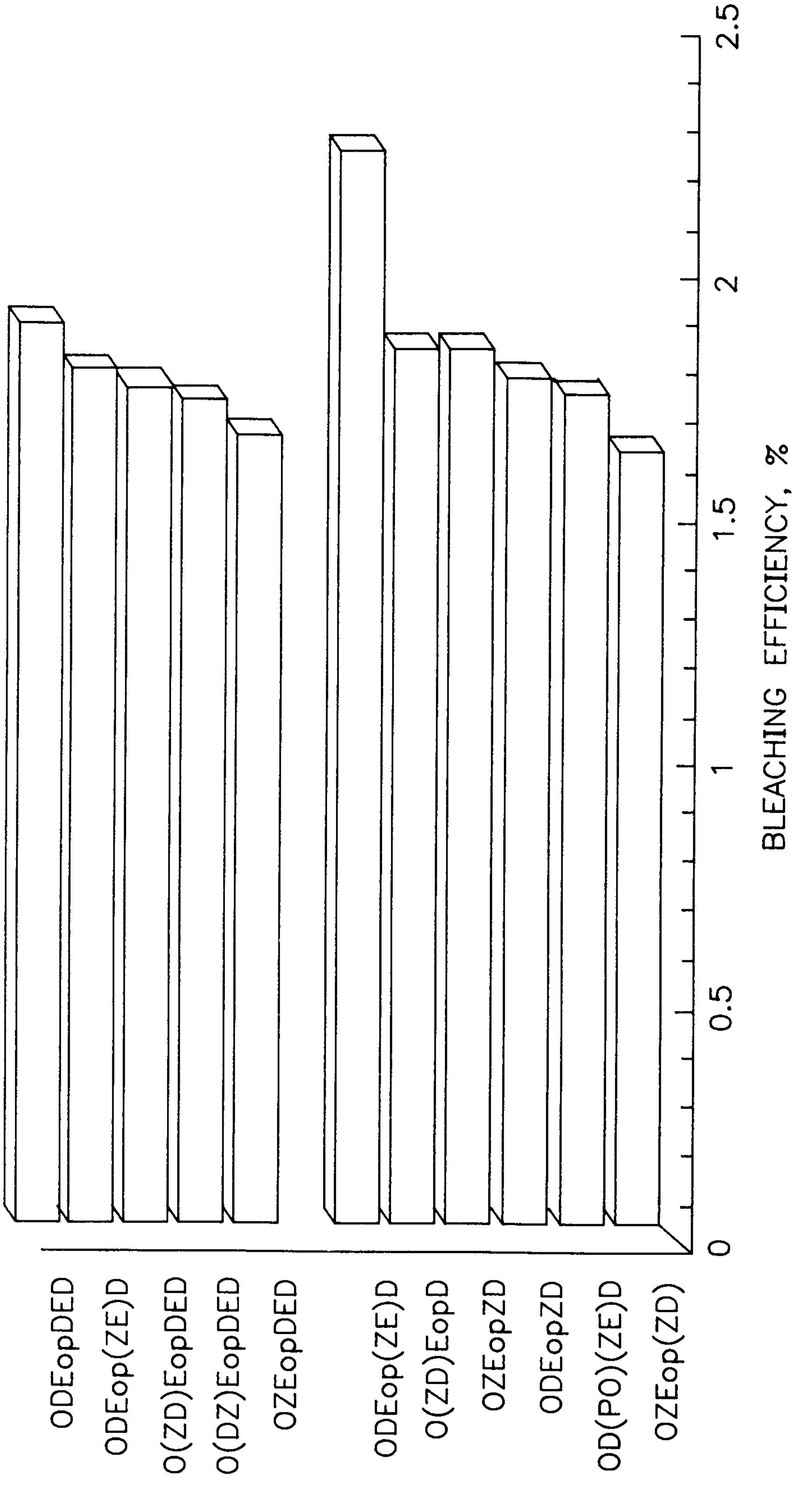
BLEACHING EFFICIENCY, %

FIG. 2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OZEopZD
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1.5
2
2.5
BLEACHING EFFICIENCY, %

FIG. 3

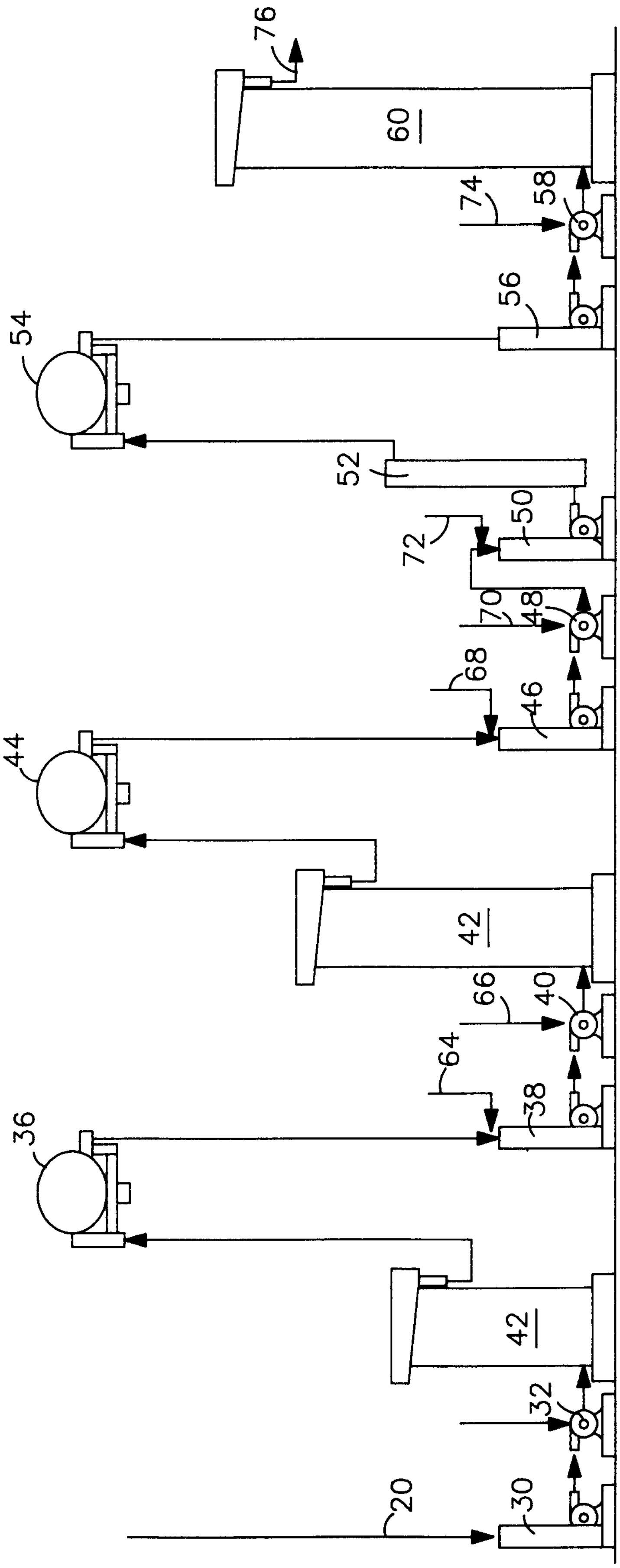

FIG. 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 11 5927

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D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	17 November 1998	Nestby, K

CATEGORY OF CITED DOCUMENTS

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