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(54) Titre : BLANCHIMENT AU DIOXYDE DE CHLORE AVEC DES ADDITIFS
 (54) Title: ADDITIVES TO CHLORINE DIOXIDE BLEACHING

(57) **Abrégé/Abstract:**

A method has been developed which enhances the effectiveness of chlorine dioxide bleaching of lignocellulosic materials, It effected by adding to the chlorine dioxide bleaching stage an aldehyde compound at a concentration of from about 0.01 % to about 20 by weight of the oven-dried lignocellulosic material.

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(54) Title: CHLORINE DIOXIDE BLEACHING WITH ADDITIVES		
<p>(57) Abstract</p> <p>A method has been developed which enhances the effectiveness of chlorine dioxide bleaching of lignocellulosic materials. It effected by adding to the chlorine dioxide bleaching stage an aldehyde compound at a concentration of from about 0.01 % to about 20 by weight of the oven-dried lignocellulosic material.</p>		

CHLORINE DIOXIDE BLEACHING WITH ADDITIVES

Technical Field

5 This invention relates to a method for delignifying and/or bleaching a lignocellulosic material, and more particularly, to a method for improving the performance of chlorine dioxide in the process of bleaching lignocellulosic pulp.

10 Background Art

Pulp mills are aggressively moving to elemental chlorine-free bleaching to address environmental and market issues. The move to chlorine dioxide virtually eliminates the formation of poly-chlorinated phenolic compounds, and substantially reduces the contributions of adsorbable organic halides (AOX), colour and chloroform in the effluent. Drawbacks of chlorine dioxide include the high cost of increased chlorine dioxide generation and the poorer bleaching performance of chlorine dioxide in the first stage (delignification) of the bleaching process when chlorine is replaced entirely by chlorine dioxide. The need for more oxidation equivalents increases the overall bleaching cost to reach a target kappa number and/or brightness.

Over the years various modifications and improvements to the basic chlorine dioxide process have been described in the technical literature. These efforts have addressed the optimization of the bleaching conditions and the optimization of the bleaching sequence configurations. However, little work has been done on enhancing chlorine dioxide bleaching through the use of additives. Dimethylsulfoxide, sulfamic acid and hydrogen

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peroxide have been tested as additives in chlorine dioxide bleaching to reduce the formation of AOX, but these additives also reduced the delignification efficiency of chlorine dioxide and increased bleaching cost to a varying degree [Y. Ni, G.J. Kubes, and A.R.P. van Heiningen, J. Pulp
5 Paper Sci., 1994, 20(4): J103-106; M.J. Joncourt, P. Froment, D. Lachenal, and C. Chirat, International Pulping Conf., Chicago, October 1-5, 1995, p 149-152; M.J. Joncourt, G. Mortha and D. Lachenal, International Symp. Wood Pulping Chemistry, Montreal, June 9-12, 1997, p J6-1 to J6-5; B.-H. Yoon and L.-J. Wang, International Pulp Bleaching
10 Conf., Helsinki, June 1-5, 1998, p 407-412]. It is known that a certain proportion of chlorine dioxide is converted to chlorite during chlorine dioxide bleaching, which may represent a loss of oxidizing power of chlorine dioxide [W.H. Rapson and C.B. Anderson, CPPA Trans. Tech., Sect., 1977, 3(2):Tr52-55 and Tappi J., 1978, 61(10):97-99; I.
15 Wartiovaara, Paperi ja Puu - Papper o. Trä, 1982, 64(9): 534-545 and 64(10): 581-584]. A two-step high-pH/low-pH method for chlorine dioxide bleaching has been proposed and tested as a means to improve the performance of the chlorine dioxide bleaching process [G.E. Seger, H. Jameel and H.-m. Chiang, Tappi J., 1992, 75(7):174-180]. The working
20 hypothesis of the two-step method is that chlorate formation can be reduced at the higher pH conditions, and the chlorite formed in the first high-pH step can become reactive in the second low-pH step [G.E. Seger, H. Jameel and H.-m. Chiang, Tappi J., 1992, 75(7):174-180; B.-H. Yoon and L.-J. Wang, International Pulp Bleaching Conf., Helsinki, June 1-5, 1998, p
25 407-412]. Iron has been tested as an additive in chlorine dioxide bleaching to regenerate chlorine dioxide from chlorite [M.J. Joncourt, G. Mortha and D. Lachenal, International Symp. Wood Pulping Chemistry, Montreal, June 9-12, 1997, p J6-1 to J6-5]. It was found, however, that iron also reacted

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with chlorine dioxide and reduced its delignification efficiency. Moreover, a significant loss of pulp viscosity was observed.

DISCLOSURE OF THE INVENTION

5 The present invention seeks to provide an improved chlorine dioxide bleaching process.

In a typical implementation of the present invention this is accomplished by enhancing the effectiveness of chlorine dioxide in reaction with
10 lignocellulosic material by carrying out the reaction in the presence of an aldehyde in the delignification and/or the bleaching stages of the bleaching process. In accordance with the method of the present invention the lignocellulosic pulp after reaction with chlorine dioxide in the presence of the aldehyde may be bleached in accordance with known bleaching and
15 extraction methods.

Thus, in accordance with the invention, the chlorine dioxide delignification and/or bleaching performance is improved, compared to the performance obtained with conventional chlorine dioxide bleaching, as evidenced by a
20 decrease in Kappa number, which is an indicator of the lignin content in pulp, an increase in brightness or both. Alternatively, one can practice the present invention by reducing the consumption of the chlorine dioxide required to reach a target kappa number and/or brightness.

25 Another object of the invention is to simplify conventional bleaching processes by using fewer bleaching stages. It has been found that a 3-stage D_0EoD_1 bleaching sequence with the first D_0 stage carried out according to the present invention can replace a 5-stage $D_0EoD_1ED_2$ sequence.

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Thus in accordance with the invention there is provided, a process for improving delignification and/or brightening during the bleaching of a lignocellulosic pulp comprising reacting the lignocellulosic pulp with chlorine dioxide in the presence of an aldehyde.

In another aspect of the invention there is provided, in a process of treating a lignocellulosic pulp with a chlorine dioxide solution to effect a reduction in Kappa number and an increase in brightness of the pulp, the improvement wherein the pulp is reacted with the chlorine dioxide solution in the presence of an aldehyde.

DESCRIPTION OF PREFERRED EMBODIMENTS

A "chlorine dioxide stage" as contemplated by the present invention can be any of the stages in a bleaching process which use chlorine dioxide. At the beginning of the sequence, the chlorine dioxide stage is typically referred to as a delignification stage, whereas in the middle or towards the end of the sequence, it is referred to as a bleaching stage.

The lignocellulosic pulps used in the method of the present invention can be derived from wood and/or non-wood derived lignocellulosic material and. This material can be treated with other known delignification, extraction, or bleaching agents before being reacted with chlorine dioxide. For example, typical stages applied to a pulp before a chlorine dioxide stage can be another chlorine dioxide stage, an alkali extraction, oxygen delignification, ozone, peroxide, peracetic acid, chelation, acid hydrolysis, enzyme treatment, applied as a single stage or as multi-stages, with or without washing between the stages.

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The chlorine dioxide solution used in the method of the present invention can be generated using known processes and may or may not contain chlorine or other chlorine species. The chlorine dioxide may be added to a stage where other delignification/bleaching agents such as chlorine or ozone are being added.

In a particular embodiment: in the chlorine dioxide stage, the lignocellulosic material is placed in a vessel or container, to which is added a solution containing chlorine dioxide and a solution containing an aldehyde compound.

The aldehyde suitably is of formula:

$RCHO$, where $R = C_nH_mO_xS_yN_z$

where n and x are each integers of from 0 to 12; m is an integer of from 1 to 24; and y and z are each integers of from 0 to 4.

In especially preferred embodiments R is H or lower alkyl of 1 to 5 carbon atoms.

This group of aldehydes includes formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde and benzaldehyde and such aldoses as glyoxal, arabinose, xylose, mannose, rhamnose, glucose, lactose, maltose and derivatives thereof which provide a source of the aldehyde or aldose, such derivatives may be added as such or formed in situ, for example, formaldehyde bisulfite.

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The reaction with chlorine dioxide is suitably conducted at a temperature within the range from about 20°C to about 100°C (or if pressurized, from 20°C to about 130°C), at a consistency from 1 to 35%, and at a pH from
5 about 1 to about 12 for a period of from about 1 minute to about 360 minutes.

The amount of chlorine dioxide added for the bleaching process expressed as active chlorine multiple (ACM), suitably is from 0.05 to 0.5. The ACM
10 is defined as the amount of chlorine dioxide being added to pulp, expressed as percent active chlorine on oven-dry pulp basis, divided by the Kappa number of the pulp entering the stage. The amount of chlorine dioxide added to the bleaching stage, expressed as percent on wt. of pulp oven-dry basis, can range from 0.05 to 10%.

15

The % consistency refers to the weight % of pulp solids in a pulp suspension.

In a preferred embodiment of the invention, the conditions in the chlorine
20 dioxide stage containing the aldehyde are a temperature of 50°C, a consistency of 3.5%, a retention time of 30 minutes and an ACM of 0.25. In another embodiment of the invention, the conditions in the chlorine dioxide stage are a temperature of 70°C, a consistency of 10%, a retention time of 180 minutes, a chlorine dioxide charge of 1.0% in a first chlorine
25 dioxide bleaching stage, and 0.3% in the second chlorine dioxide bleaching stage.

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The aldehyde can be added as a part of the chlorine dioxide solution, as a part of the filtrates used as make-up liquor in the bleaching process, or in a separate addition. It can also be added as part of the pulp carryover from a previous stage. Benefit can also arise from adding the aldehyde after a first
5 initial reaction of the chlorine dioxide with the lignocellulosic material.

The amount of the aldehyde compound added to the chlorine dioxide stage can be from about 0.01% to about 20%, by wt., based on the oven-dried wt. of the lignocellulosic pulp employed. It is preferred however, to employ
10 from about 0.02% to about 5% based on the oven-dried wt. of the lignocellulosic pulp. The preferred aldehyde is formaldehyde and lower alkyl aldehydes having from 1 to 5 carbons atoms in the alkyl moiety, which may or may not contain sulphur and nitrogen.

15 The lignocellulosic pulps after bleaching with chlorine dioxide in accordance with the method of the present invention may then be bleached in accordance with any of the known bleaching methods including any of the known alkaline extraction methods.

20 In order to disclose more clearly some of the nature of the aforementioned embodiments of the present invention, the following examples are presented.

EXAMPLES

Example 1

5

An unbleached hardwood kraft pulp with a kappa number of 12.0 was bleached using a D₀E sequence where D₀ represents a chlorine dioxide bleaching stage and E represents an alkaline extraction stage. Different amounts of formaldehyde were added to the D₀ stage.

10

The chlorine dioxide stage was carried out by placing the pulp in a vessel, and mixing appropriately heated water into the pulp and adjusting the pH to 3.0 using sulphuric acid. A formaldehyde solution was rapidly mixed into the pulp slurry, followed immediately by a rapid addition of the chlorine dioxide solution. The container was then closed, and mixed vigorously to disperse the solution thoroughly. The charge of chlorine dioxide added to the pulp slurry was set at 1.14% based on weight of oven-dry pulp, which is equivalent to an active chlorine multiple (ACM) of 0.25. The active chlorine multiple is defined as the amount of chlorine dioxide being added to pulp, expressed as active chlorine divided by the Kappa number of the pulp entering the stage. The charge of formaldehyde added to the chlorine dioxide stage ranged from 0 to 0.6% based on weight of oven-dry pulp. The pulp consistency was 3.5%, the reaction temperature was 50°C, and the reaction time was 30 minutes. After the reaction, the pulp was thoroughly washed with water to remove the reaction by-products.

25

The extraction (E) stage was carried out as a pulp slurry having a 10% consistency, a temperature of 70°C, and a reaction time of 60 minutes. The

charge of NaOH was 1.0% based on the wt. of oven-dried pulp. After the extraction the pulp was, once again, thoroughly washed.

It is readily evident from an examination of the results in Table I, that the
 5 Kappa number of the washed pulp after the D₀ stage and the E stage was lower when formaldehyde was used, showing that the performance of the chlorine dioxide stage was increased.

TABLE 1

10

Experiment number (D ₀ E sequence)	1	2	3	4
Chlorine dioxide added in D ₀ as active chlorine multiple (ACM) % on wt. of o.d. pulp	0.25 1.14	0.25 1.14	0.25 1.14	0.25 1.14
Formaldehyde added in D ₀ % on wt. of o.d. pulp	0	0.04	0.1	0.6
Kappa number after D ₀	5.6	5.3	5.0	4.7
Kappa number after D ₀ E	4.5	4.2	3.9	3.5

Example 2

An unbleached hardwood kraft pulp with a kappa number of 12.0 was bleached using a D₀E₀D₁ED₂ bleaching sequence. E₀ represents an alkaline extraction stage fortified with oxygen. The D₀ stage was carried out with and without formaldehyde.

The first chlorine dioxide stage (D₀) was carried out using the procedure employed in Example 1, with an active chlorine multiple (ACM) of 0.30 which represents a charge of 1.37% ClO₂ based on wt. of oven-dry pulp. The second (D₁) and third (D₂) chlorine dioxide stages were carried out using the same procedure as described for the D₀ stage, except that the pH was not adjusted and formaldehyde was not employed. The reaction conditions for the D₁ stage were: consistency 10%, reaction temperature 70°C, and reaction time 150 minutes. The charges of chlorine dioxide and NaOH in D₁ were 0.8 and 0.4% respectively, based on wt. of oven-dried pulp. The reaction conditions for the D₂ stage were consistency 10%, reaction temperature 70°C, and reaction time 180 minutes. The charge of chlorine dioxide in the D₂ stage was 0.15% based on wt. of oven-dried pulp.

The extraction stage fortified with oxygen (E₀) was carried out at 10% consistency in a laboratory pressurized peg mixer maintained at 0.14 MPa oxygen pressure for the first 10 minutes of the reaction, and at atmospheric pressure for 50 minutes. The reaction temperature was maintained at 70°C. The conventional extraction stage (E) was carried out using the procedure employed in Example 1, except that the charge of NaOH was 0.5% based on wt. of oven-dried pulp.

The bleaching results are shown in Table II. Compared to conventional chlorine dioxide bleaching the present invention using formaldehyde in the D₀ stage provides a lower kappa number after D₀Eo and a higher final
5 brightness after D₀EoD₁ED₂.

TABLE II

Experiment number (D ₀ EoD ₁ ED ₂ sequence)	1	2
Chlorine dioxide added in D ₀ ' as active chlorine multiple (ACM) % on wt. of o.d. pulp	0.30 1.37	0.30 1.37
Formaldehyde added in D ₀ ' % on wt. of o.d. pulp	0	0.6
Kappa number after D ₀ Eo	4.1	2.6
ISO brightness after D ₀ EoD ₁ ED ₂ , %	88.1	89.1
b* value after D ₀ EoD ₁ ED ₂	4.1	3.8

10

Example 3

An unbleached softwood kraft pulp with a kappa number of 31.3 was bleached using a D₀EoD₁ED₂ bleaching sequence. The D₀ stage was
15 carried out with and without formaldehyde.

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The chlorine dioxide charges in the $D_0EoD_1ED_2$ sequence were as follows: 3.57% in the D_0 stage (0.30 ACM); 0.8%, 1.3% and 1.8% in the D_1 stage; and 0.3% in the D_2 stage. The charges of NaOH were as follows: 3.3% in the Eo stage; from 0.3 to 0.94% in the D_1 stage, and 0.5% in the E stage.

5 All chemical charges are expressed as percent on pulp, oven-dry basis.

The bleaching results are shown in Table III. Compared to conventional chlorine dioxide bleaching, the present invention using formaldehyde in the D_0 stage provides a lower kappa number after D_0Eo and a higher final
10 brightness after $D_0EoD_1ED_2$. Surprisingly, it also allows a 3-stage sequence to achieve the same brightness as a 5-stage sequence.

TABLE III

Experiment Number (D ₀ EoD ₁ ED ₂ sequence)	1			2		
Chlorine dioxide added in D ₀ ' as active chlorine multiple (ACM) on wt. of o.d. pulp basis	0.30 3.57			0.30 3.57		
Formaldehyde added in D ₀ ' % on wt. of o.d. pulp basis	0			2.6		
Kappa number after D ₀ Eo	3.3			2.4		
Chlorine dioxide charge in D ₁ ' % on wt. of o.d. pulp basis	0.8	1.3	1.8	0.8	1.3	1.8
ISO brightness after D ₀ EoD ₁ ' %	87.5	89.0	89.5	88.8	90.2	90.6
Chlorine dioxide charge in D ₂ ' % on wt. of o.d. pulp basis	0.3	0.3	0.3	0.3	0.3	0.3
ISO Brightness after D ₀ EoD ₁ ED ₂ , %	90.5	91.2	91.5	91.7	91.8	92.0

5

Example 4

An oxygen-delignified softwood kraft pulp with a kappa number of 16.8 was bleached using a D₀EoD₁ED₂ bleaching sequence. The D₀ stage was carried out with and without formaldehyde.

10

The chlorine dioxide charges in the D stages of the D₀EoD₁ED₂ sequence were as follows: 1.92% in the D₀ stage (0.30 ACM); 0.5%, 1.0%, and 1.5%

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in the D₁ stage; and 0.3% in the D₂ stage. The charge of NaOH was as follows: 1.9% in the E₀ stage; from 0.20 to 0.65% in the D₁ stage; and 0.5% in the E stage. All percentages are based on the weight of oven-dried pulp.

5

The bleaching results are shown in Table IV. Compared to conventional chlorine dioxide bleaching, the present invention using formaldehyde in the D₀ stage provides a lower kappa number after D₀E₀ and a higher final brightness after D₀E₀D₁E₀D₂.

TABLE IV

Experiment number (D ₀ EoD ₁ ED ₂ sequence)	1			2		
Chlorine dioxide added in D ₀ ' as active chlorine multiple (ACM) % on wt. of o.d. pulp	0.30 1.92			0.30 1.92		
Formaldehyde added in D ₀ , % on wt. of o.d. pulp	0			1.5		
Kappa number after D ₀ Eo	3.5			2.6		
Chlorine dioxide charge in D ₁ ' % on wt. of o.d. pulp	0.5	1.0	1.5	0.5	1.0	1.5
ISO brightness after D ₁ , %	83.0	86.6	87.7	85.0	88.1	88.8
Chlorine dioxide in D ₂ ' % on wt. of o.d. pulp	0.3	0.3	0.3	0.3	0.3	0.3
ISO brightness after D ₀ EoD ₁ ED ₂ , %	88.9	90.3	90.8	90.4	91.3	91.5

5 Example 5

An oxygen delignified softwood kraft pulp with a kappa number of 16.8 was bleached using a D₀ED₁ and a D₀EpD₁ bleaching sequence. The D₀ stage was carried out with and without formaldehyde.

10

The chlorine dioxide charges were as follows: 1.92% in the D₀ stage (0.30 ACM); and 1.5% in the D₁ stage. The charges of NaOH were as follows: 1.9% in the E stage; and 0.7% in the D₁ stage. All percentages are based on the wt. of oven-dried pulp. The peroxide charge in the Ep stage was 1.0%.

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The bleaching results are given below in Table V. Compared to conventional chlorine dioxide bleaching, the present invention using formaldehyde in the D₀ stage provides a lower kappa number after D₀E and D₀Ep and a higher final brightness after D₀ED₁ and D₀EpD₁.

TABLE V

Experiment number (D ₀ ED ₁ or D ₀ EpD ₁ sequence)	1		2	
Chlorine dioxide added in D ₀ ' as active chlorine multiple (ACM) % on wt. of o.d. pulp	0.30 1.92		0.30 1.92	
Formaldehyde added in the D ₀ stage, % on wt. of o.d. pulp	0		1.5	
Kappa number after D ₀ E	4.9	-	3.2	-
Kappa number after D ₀ Ep	-	3.4	-	2.0
Chlorine dioxide charge in D ₁ ' % on wt. of o.d. pulp	1.5	1.5	1.5	1.5
ISO brightness after D ₀ ED ₁ or D ₀ EpD ₁ , %	85.2	88.6	87.4	90.1

Example 6

An unbleached softwood kraft pulp with a kappa number of 26.4 was bleached using a D₀Ep sequence where D₀ represents a chlorine dioxide
5 bleaching stage and Ep represents an alkaline extraction stage fortified with hydrogen peroxide (H₂O₂). Either formaldehyde or glyoxal or a mixture comprising both formaldehyde and glyoxal was added to the D₀ stage.

The chlorine dioxide stage was carried out using the procedure employed in
10 Example 1, with an ACM of 0.30 which represents a charge of 3.01% ClO₂ based on wt. of oven-dry pulp. A solution of formaldehyde or glyoxal at a charge of 1.13% based on wt. of oven-dry pulp or a mixture of formaldehyde and glyoxal at a charge of 0.56 and 0.57%, respectively, each based on wt. of oven-dry pulp was added to the pulp slurry followed by a
15 rapid addition of the chlorine dioxide solution. The reaction conditions in the D₀ stage were: consistency, 3.5%, 55°C and a reaction time of 30 minutes. After the reaction, the pulp was thoroughly washed with water to remove the reaction by-products.

20 The extraction (Ep) stage was carried out as a pulp slurry having a 10% consistency, a temperature of 90°C, and a reaction time of 60 minutes. The charge of NaOH was 1.8% and the charge of H₂O₂ was 0.3%, each based on the wt. of oven-dried pulp. After the extraction the pulp was, once again, thoroughly washed.

25

It is readily evident from an examination of the results in Table VI, that the Kappa number of the washed pulp after the D₀ stage and the Ep stage was lower when formaldehyde or glyoxal or a mixture of formaldehyde and

glyoxal was used, showing that the performance of the chlorine dioxide stage was improved.

5

TABLE VI

Experiment number (D ₀ Ep sequence)	1	2	3	4
Chlorine dioxide added in D ₀ as active chlorine multiple (ACM) % on wt. of o.d. pulp	0.30 3.01			
Formaldehyde added in D ₀ , % on wt. of o.d. pulp	0	1.13	0	0.56
Glyoxal added in D ₀ , % on wt. of o.d. pulp	0	0	1.13	0.57
Kappa number after D ₀ Ep	4.2	3.6	3.5	3.6

Example 7

An unbleached hardwood kraft pulp with a kappa number of 12.0 was
5 bleached using a D₀E₀ sequence. The D₀ stage was carried out with either
formaldehyde bisulphite or glucose.

The first chlorine dioxide stage (D₀) was carried out using the procedure
employed in Example 2, with an active chlorine multiple (ACM) of 0.25
10 which represents a charge of 1.14% ClO₂ based on wt. of oven-dry pulp.
Either formaldehyde bisulphite at a charge of 0.6% or glucose at a charge
of 0.8%, each based on wt. of oven-dry pulp, was applied in the chlorine
dioxide stage.

15 The extraction stage fortified with oxygen (E₀) was carried using the same
procedure and conditions employed in Example 2.

It is readily evident from an examination of the results in Table VII, that,
compared to conventional D₀E₀ bleaching, the present invention using
20 either formaldehyde bisulphite or glucose in the D₀ stage results in a lower
kappa number after the D₀ stage and the E₀ stage.

TABLE VII

Experiment number (D ₀ Eo sequence)	1	2	3
Chlorine dioxide added in D ₀ as active chlorine multiple (ACM) % on wt. of o.d. pulp		0.25 1.14	
Formaldehyde bisulphite added in D ₀ , % on wt. of o.d. pulp	0	0.6	0
Glucose added in D ₀ , % on wt. of o.d. pulp	0	0	0.8
Kappa number after D ₀	5.6	5.1	5.2
Kappa number after D ₀ Eo	4.5	4.0	3.9

5 Example 8

An unbleached softwood kraft pulp which had been delignified with oxygen to a kappa number of 16.6 was bleached in a D₀EoD₁ sequence. The D₁ stage was carried with and without glyoxal.

10

The chlorine dioxide charges in the D₀EoD₁ sequence were as follows: 1.39% (0.22 ACM) in the D₀ stage and 1.0% in the D₁ stage. The charges of NaOH were as follows: 1.46% in the Eo stage; and 0.60-0.65% in the D₁

stage. All chemical charges are expressed as percent on pulp, oven-dry basis. The procedures employed in the D₀ and the D₁ stages in the E₀ stage are described in Example 2.

- 5 It is readily evident from an examination of the results in Table VIII, that the present invention using glyoxal in the D₁ stage provides a pulp with a higher final brightness.

10

TABLE VIII

Experiment number (OD ₀ E ₀ D ₁ sequence)	1	2
Chlorine dioxide added in D ₀ as active chlorine multiple (ACM) % on wt. of o.d. pulp	0.22 1.39	
Extraction stage (E ₀), NaOH, % on wt. of o.d. pulp Kappa number	1.46 4.1	
Chlorine dioxide stage (D ₁), ClO ₂ , % on wt. of o.d. pulp Glyoxal added in D ₁ , % on wt. of o.d. pulp ISO brightness, %	1.0 0 83.1	1.0 0.1 84.8

CLAIMS:

1. A process for improving delignification and/or brightening during the bleaching of a lignocellulosic pulp with chlorine dioxide comprising adding a chlorine dioxide solution to the lignocellulosic pulp, reacting the pulp with the chlorine dioxide in the presence of an aldehyde to produce a pulp characterized by at least one of lower kappa and higher brightness, than is achieved by the chlorine dioxide in the absence of the aldehyde.
2. A process according to claim 1, wherein said aldehyde is formaldehyde.
3. A process according to claim 1, wherein said aldehyde is an aldose.
4. A process according to claim 1, wherein said aldehyde is of general formula:



in which:



wherein

- n is an integer of 0 to 12,
- x is an integer of 0 to 12,
- m is an integer of 1 to 24,
- y is an integer of 0 to 4, and
- z is an integer of 0 to 4.

5. A process according to claim 4, wherein R is alkyl of 1 to 5 carbon atoms.

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6. A process according to claim 1, 2, 3, 4 or 5, wherein the reacting is carried out at a temperature of 20°C to 130°C, at a pulp consistency of 1 to 35%, by weight, at a pH of 1 to 12 for a period of 1 to 360 minutes.
- 5 7. A process according to claim 1, 2, 3, 4, 5 or 6, wherein the chlorine dioxide is reacted at an Active Chlorine Multiple of 0.05 to 0.5.
8. A process according to any one of claims 1 to 7, wherein said aldehyde is present in an amount of 0.01% to 20%, by weight, based on the
10 oven-dried weight of the pulp.
9. A process according to any one of claims 1 to 6, wherein the chlorine dioxide is reacted at an Active Chlorine Multiple of 0.05 to 0.5 and said aldehyde is present in an amount of 0.02% to 5%, by weight,
15 based on the oven-dried weight of the pulp.
10. A process according to any one of claims 1 to 9, wherein said reacting is in a chlorine dioxide stage of a multi-stage bleaching process.
- 20 11. A process according to claim 10, wherein said multi-stage bleaching process has a D₀E sequence, and said reacting is in the D₀ stage.
12. A process according to claim 10, wherein said multi-stage bleaching process has a D₀EoD₁ED₂ sequence and said reaction is in at least one of
25 the D₀, D₁ and D₂ stages.

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13. A process according to claim 12, wherein said reaction is in the D₀ stage.
14. A process according to claim 1, for treating said lignocellulosic pulp to effect a reduction in Kappa number and an increase in brightness of the pulp.
15. A process according to claim 14, wherein the aldehyde is formaldehyde.
- 10 16. A process according to claim 14 or 15, wherein the pulp is reacted with the chlorine dioxide solution in the D₀ stage of a D₀EoD₁ bleaching sequence.
- 15 17. A process according to claim 14 or 15, wherein the pulp is reacted with the chlorine dioxide solution in the D₀ stage of a D₀EoD₁ED₂ bleaching sequence.
- 20 18. A process according to claim 14 or 15, wherein the pulp is reacted with the chlorine dioxide solution in the D₁ stage of a D₀EoD₁ bleaching sequence.
- 25 19. A process according to claim 14 or 15, wherein the pulp is reacted with the chlorine dioxide solution in the D₁ stage of a D₀EoD₁ED₂ bleaching sequence.

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20. A process according to claim 14 or 15, wherein the pulp is reacted with the chlorine dioxide solution in the D₂ stage of a D₀EoD₁ED₂ bleaching sequence.
- 5 21. A process according to claim 14 or 15, wherein the pulp is reacted with said chlorine dioxide together with chlorine or ozone.