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(54) **Process for the bleaching of mechanical paper pulp**

(57) The invention is related to a process for the bleaching of mechanical paper pulp with one or more peroxide oxidizing agents, in which the pulp is pretreated in a pretreatment step with one or more chelating agents chosen from aspanic acid and its derivatives, substituted nn the nitrogen atom, characterized in that the initial pH ofthe pretreatment step, just before adding the one or more chelating agents, is above 8.

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Description

[0001] The present invention is related to a process for the bleaching of mechanical paper pulp with one or more peroxide oxidizing agents, in which the paper pulp is pretreated with a chelating agent.

[0002] It is known to bleach paper pulp with peroxide oxidizing agents such as peracids, or hydrogen peroxide.

[0003] It is also known to proceed to a pretreatment step of the paper pulp with a chelating agent, in order to selectively eliminate metallic ions detrimental to bleaching. Indeed, some metallic ions catalyze decomposition reactions of the peroxide compounds. The most detrimental ions are manganese, iron, and copper.

[0004] Powerful chelating agents can be of the aminocarboxylic type, such as ethylene diamine tetra-acetic acid and its salts (EDTA), or diethylene triamine penta-acetic acid and its salts (DTPA). Nevertheless, these chelating agents are poorly biodegradable which can generate environmental problems.

[0005] The use of biodegradable chelating agents such as aspartic acid and its derivatives, substituted on the nitrogen, is described in the international application WO 97/30209. Such products include ethylenediamine-N,N'-disuccinic acid (EDDS) and 2,2'-imino-disuccinic acid (IDS). In that previous application, the pretreatment step is conducted at a pH from 4 to 8. A first disadvantage of this process is that it does not conduct to an optimal brightness of the paper pulp. A second disadvantage is that the pH of the pretreatment step must be measured and maintained in a range from 4 to 8 during the whole step.

[0006] The international application WO 99/464.41 describes a process for the bleaching of mechanical paper pulp with one or more peroxide oxidizing agents, in which the pulp is pretreated with one or more chelating agents chosen from aspartic acid and its derivatives, substituted on the nitrogen, and at a pH above 8. As in the previous invention, the pH of the pretreatment step must be measured during the whole step and must be maintained above 8.

[0007] The purpose of the present invention is to provide a simplified bleaching process, avoiding measurement and control of the pH during the pretreatment step, conducting to an optimal brightness of the paper pulp, while still using biodegradable chelating agents during the pretreatment step.

[0008] The present invention therefore relates to a process for the bleaching of mechanical paper pulp with one or more peroxide oxidizing agents, in which the pulp is pretreated in a pretreatment step with one or more chelating agents chosen from aspartic acid and its derivatives, substituted on the nitrogen atom, characterized in that the initial pH of the pretreatment step, just before adding the one or more chelating agents, is above 8.

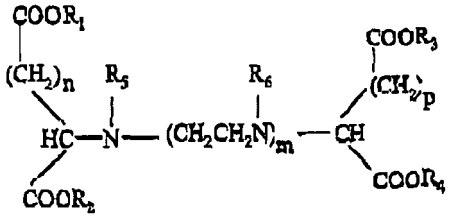
[0009] One of the essential features of the present invention resides in solely controlling the initial pH of the pretreatment step, which must be above 8 just before adding the one or more chelating agents, and not measuring it after the addition of the chelating agent, and so until the end of the pretreatment step. It has indeed surprisingly been found that, as the critical pH of the pretreatment step is its initial pH, it is therefore not necessary to control it anymore during the rest of the pretreatment step. This is important as it is known that, due to alkaline demand of the paper pulp, the pH will naturally decrease with time. According to this invention, it is not necessary to measure it during the pretreatment step, nor to keep it above 8 by the addition of pH modifying compounds. It follows therefrom that the pretreatment step of the process is advantageously simplified.

[0010] By mechanical paper pulps are meant paper pulps obtained by mechanical treatment. Examples of such paper pulps are pressure groundwood (PGW), stone groundwood (SGW), thermomechanical pulp (TMP), refiner mechanical pulp (RMP), chemithermomechanical pulp (CRMP) and alkaline peroxide mechanical pulp (APMP or APP).

[0011] By initial pH of the pretreatment step is meant the pH of the paper pulp just before the addition of one or more chelating agents. The pH is measured using equipment normally found in pulp mills for such a purpose.

[0012] By control of pH is meant the adjustment of the pH to a certain value. This can be done by means of pH modifying compounds. Examples of such compounds are caustic soda (NaOH) or suitable alternative bases. Usually, these compounds are alkalis because the natural pH of mechanical pulps is generally lower than the one required in practice for efficient control of metal ions.

[0013] In the process of the invention, the chelating agent used in the pretreatment step is chosen from aspartic acid and its derivatives, substituted on the nitrogen. The chelating agent can particularly be chosen from N-carboxymethyl-aspartic acid, N-(1,2-dicarboxyethyl)-aspartic acid, N-(1,2-dicarboxy-2-hydroxyethyl)-aspartic acid, and compounds according to the formula:



where n is 1-3, m is 0-3, p is 1-3, R_1, R_2, R_3 and R_4 are H, Na, K, Ca or Mg, R_5 and R_6 are H, CH_2OH, CH_2CH_2OH or $CH_2O(CH_2CH_2O)_{1-10}CH_2CH_2OH_3$ and mixtures thereof. An especially suitable chelating agent is, for example, ethylenediamine-N,N'-disuccinic acid (EDDS), its various isomers or its alkali metal salts or its earth-alkali metal salts. Another especially suitable chelating agent is 2,2'-iminodisuccinic acid (IDS), its various isomers or its alkali metal salts or its earth-alkali metal salts.

[0014] In the process of the invention, good results are obtained using only one chelating agent. Nevertheless, more than one chelating agent can be used. For example, several chelating agents according to the invention can be combined. A chelating agent according to the invention can also be combined with one or more conventional chelating agents such as aminocarboxylated chelating agents such as EDTA or hydroxycarboxylated chelating agents such as glucaric acid.

[0015] In the process of the invention, the paper pulp is pretreated with one or more chelating agents at an initial pH of at least 8,1. The pH is in most cases maximum 11. Within this range, the optimum must be established for each particular pulp. For some pulps, the optimal pH is for example equal to or higher than 8,5. For some others, the optimal pH is equal to or higher than 9, and for others it is equal to or higher than 10.

[0016] In the process of the invention, the pretreatment step with one or more chelating agent is usually carried out at the temperature generated by the mechanical treatment of the wood. The temperature can vary widely and is usually at least 40°C. It is generally less than or equal to 95°C. The temperature may vary from 40 to 95°C.

[0017] In the process of the invention, the pretreatment step with one or more chelating agent is carried out in the presence of water in order to reach a consistency of at least 1% by weight of dry paper pulp. The consistency of the paper pulp is usually less than or equal to 50% by weight of dry paper pulp. The consistency of the paper pulp can be highly variable within the range from 1 to 50% by weight of dry paper pulp and will be adapted to the type of equipment available for mixing the chelating agents into the process. In the majority of the cases, a consistency of less than or equal to 10% by weight of dry paper pulp, for instance from 3 to 4% by weight of dry paper pulp, will be suitable. In special cases, higher values, up to 45% by weight of dry paper pulp can be used.

[0018] In the process of the invention, the chelating agent used in the pretreatment step is used at a concentration by weight of dry paper pulp of at least 0,1 %. The concentration of the chelating agent by weight of dry paper pulp is usually less than or equal to 1,5%. The concentration of the chelating agent is highly variable within this range and must be optimized, depending on the paper will. Typical values range from 0,2 to 1,0% by weight of dry paper pulp.

[0019] It is recommended to have a good mixing of the paper pulp with the chelating agent during the pretreatment step. This can be done by introducing the chelating agent via the pump circulating the pulp through the paper mill.

[0020] The duration of the pretreatment step with one or more chelating agent is usually from 5 to 120 minutes, varying from mill to mill. Good results are obtained provided the duration of the pretreatment step is of at least 5 minutes duration before the washing step.

[0021] In the process of the invention, the oxidizing agent used in the bleaching step is usually chosen from hydrogen peroxide, organic peracids such as peracetic acid, and/or a combination thereof. The oxidizing agent is preferably hydrogen peroxide, which is advantageously used in an alkaline medium.

[0022] A washing step is usually conducted between the pretreatment step with one or more chelating agent and the bleaching step with a peroxide oxidizing agent.

[0023] Other steps, such as additional bleaching steps, can be added to the process. Nevertheless, only a pretreatment step, a washing step and a bleaching step with one or more peroxide oxidizing agents is usually sufficient for the bleaching of mechanical paper pulp.

[0024] The present invention is further illustrated with some examples below, without limiting the scope thereto.

Examples

[0025] In the examples according to the invention, the pretreatment step is conducted at a pH above 8. In the comparative examples, the pretreatment step is conducted at a pH between 4 and 8, according to the international application WO 97/30209.

[0026] The pH was measured with a Knick Portamess pH-meter (911 pH), with an Ag/AgCl electrode (Mettler Toledo,

U402-S7/120). The electrolyte was a mixture KCl / AgCl 3M. The temperature was compensated with a Knick Pt1000 (ZU0156) probe. The pH-meter was calibrated with buffer solutions from Mettler Toledo (pH 7,00 buffer with the reference 9865 and pH 4,01 buffer with the reference 9863).

[0027] The brightness of paper pulp was measured using a Datacolor Elrepho spectrophotometer (SF450) according to the ISO standard 2470.

Example 1 (according to the invention), C2 & C3 (comparative)

[0028] A mechanical paper pulp (TMP) with an initial brightness of 55.5 °ISO was pretreated with EDDS, diluted with water prior to thickening, then submitted to a bleaching process with hydrogen peroxide,

[0029] The pretreatment step was carried out at 60°C, during 20 minutes, at a consistency of 10% by weight of dry pulp and with a concentration of 0,3% in RDDS. Initial pH of the pretreatment step of examples 1, C2 and C3 was respectively 9,8, 6,0 and 5,0. The pH was measured with the standard laboratory glass electrode described above. The pH was not measured nor adjusted after the addition of the chelating agent, until the end of the pretreatment step.

[0030] The washing step was carried out by diluting the pulp to 4% consistency with water and then thickening it with a press to a consistency around 20%.

[0031] The bleaching step was carried out at 70°C, during 120 minutes, at a consistency of 15% by weight of dry pulp, with a bleach liquor containing 3 % hydrogen peroxide, 2.3% NaOH, and 2% sodium silicate by weight of dry pulp.

[0032] Brightness results are given in the table below.

Example	Chelating agent used in the pretreatment step	Initial pH	Brightness (°ISO)	Gain (°ISO)	Gain (%)
1	EDDS	9,8	69.0	13,5	24.3
C2	EDDS	6,0	67,5	12,0	21,6
C3	EDDS	5,0	59,4	3,9	7,0

Example 4 (according to the invention), C5, C6 & C7 (comparative)

[0033] respectively 9,0, 7,0, 6,0 and 5,0. The pH was measured with the standard laboratory glass electrode described above. The pH was not measured nor adjusted after the addition of the chelating agent, until the end of the pretreatment step.

[0034] The washing step was carried out as in Examples 1, C2 and C3.

[0035] The bleaching step was carried out at 70°C, during 120 minutes, at a consistency of 15% by weight of dry pulp, with a bleach liquor containing 3% hydrogen peroxide, 2.08% NaOH, and 2% sodium silicate by weight of dry pulp.

[0036] Brightness results are given in the table below.

Example	Chelating agent used in the pretreatment step	Initial pH	Brightness (°ISO)	Gain (°ISO)	Gain (%)
4	IDS	9,0	67,6	10,7	18,8
C5	IDS	7,0	63,7	6,8	12,0
C6	IDS	6,0	62,3	5,4	9,5
C7	IDS	5,0	62,8	5,9	10,4

Example 8, 9 (according to the invention), C10 & C11 (comparative)

[0037] A mechanical paper pulp (PGW) with an initial brightness of 65,6 °ISO was pretreated with EDDS, washed as per the process in Examples 1, C2 and C3, then submitted to a bleaching process with hydrogen peroxide.

[0038] The pretreatment step was carried out at 60°C, during 20 minutes, at a consistency of 10% by weight of dry pulp and with a concentration of 0.5% in EDDS. Initial pH of the pretreatment step of examples 8, 9, C10 and C11 were respectively 10,9, 9,5, 6,9 and 5,1. The pH was measured with the standard laboratory glass electrode described above. The pH was not measured nor adjusted after the addition of the chelating agent, until the end of the pretreatment step.

[0039] The washing step was carried out as in Examples 1, C2 and C3.

[0040] The bleaching step was carried out at 70°C, during 120 minutes, at a consistency of 15% by weight of dry pulp,

with a bleaching liquor containing 3% hydrogen peroxide, 1.8% NaOH, and 1,5% sodium silicate by weight of dry pulp.

[0041] Brightness results are given in the table below.

Example	Chelating agent used in the pretreatment step	Initial pH	Final pH	Brightness (°ISO)	Gain (°ISO)	Gain (%)
8	EDDS	10,9	9,6	78,8	13,2	20,1
9	EDDS	9,5	7,8	79,2	13,6	20,7
C10	EDDS	6,9	6,5	76,0	10,4	15,8
C11	EDDS	5,1	5,7	71,6	6,0	9,1

[0042] The final pH is the pH of the reacting medium at the end of the pretreatment step.

Example 12 to 16 (according to the invention)

[0043] After the pH optimization done with examples 8, 9, C10 and C11, the dosage of EDDS was optimized on the same paper pulp as the one used in these examples (initial brightness of 65.6°ISO).

[0044] The following results were obtained at a pH of 9,5, with respectively 0, 0,2, 0,4, 0,6 and 0,8% of EDDS by weight of dry pulp. The other conditions are the same as in examples 8, 9, C10 and C11.

Example	Concentration of EDDS used in the pretreatment step	Brightness (°ISO)	Gain (°ISO)	Gain (%)
12	0	69,7	4,1	6,2
13	0,2	77,8	12,2	18.6
14	0,4	79,1	13,4	20,5
15	0,6	79,0	13,4	20,5
16	0,8	79,2	13,6	20,7

Example 17, 18 (according to the invention), C19 & C20 (comparative)

[0045] A mechanical paper pulp (PGW) with an initial brightness of 67,0°ISO was pretreated with IDS, washed as per the process in Examples 1, C2 and C3, then submitted to a bleaching process with hydrogen peroxide.

[0046] The pretreatment step was carried out at 60°C, during 20 minutes, at a consistency of 10% by weight of dry pulp and with a concentration of 0.5% in IDS. Initial pH of the pretreatment step of examples 17, 18, C19 and C20 were respectively 11,0, 9,0, 7,1 and 5,1. The pH was measured with the standard laboratory glass electrode described above. The pH was not measured nor adjusted after the addition of the chelating agent, until the end of the pretreatment step.

[0047] The washing step was carried out as in Examples 1, C2 and C3.

[0048] The bleaching step was carried out at 70°C, during 120 minutes, at a consistency of 15% by weight of dry pulp, with a bleaching liquor containing 3% hydrogen peroxide, 1.8% NaOH, and 1,5% sodium silicate by weight of dry pulp.

[0049] Brightness results are given in the table below.

Example	Chelating agent used in the pretreatment step	Initial pH	Final pH	Brightness (°ISO)	Gain (°ISO)	Gain (%)
17	IDS	11,0	9,2	76,7	9,7	14,5
18	IDS	9,0	8,1	78,2	11,2	16,8
C19	IDS	7,1	6,97	77,0	10,0	15,0
C20	IDS	5,1	5,30	13,6	6,6	9,9

[0050] The final pH is the pH of the reacting medium at the end of the pretreatment step.

Example 21 to 25 (according to the invention)

[0051] After the pH optimization done with examples 17, 18, C19 and C20, the dosage of IDS was optimized on the same paper pulp as the one used in these examples (initial brightness of 67,0°ISO).

[0052] The following results were obtained at a pH of 9,0, with respectively 0, 0,2, 0,4, 0,6 and 0,8% of IDS by weight of dry pulp. The other conditions are the same as in examples 17, 18, C19 and C20.

Example	Concentration of IDS used in the pretreatment step	Brightness (°ISO)	Gain (°ISO)	Gain (%)
21	0	70,1	3,1	4,6
22	0,2	75,6	8,6	12,8
23	0,4	77,2	10,2	15,2
24	0,6	77,7	10,7	16,0
25	0,8	78,2	16,7	16,7

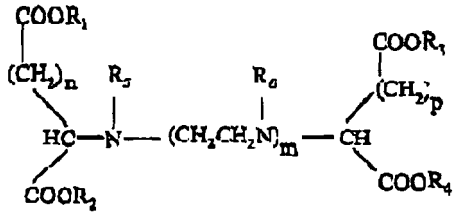
Claims

1. Process for the bleaching of mechanical paper pulp with one or more peroxide oxidizing agents, in which the pulp is treated in a pretreatment step with one or more chelating agents chosen from aspartic acid and its derivatives, substituted on the nitrogen atom, **characterized in that** the initial pH of the pretreatment step, just before adding the one or more chelating agents, is above 8.

2. Process according to claim 1, **characterized in that** the pH of the pretreatment step is not measured between the addition of one or more chelating agents, and the end of the pretreatment step.

3. Process according to claims 1 and 2, **characterized in that** the pH is not controlled by the addition of pH modifying compounds during the pretreatment step.

4. Process according to claims 1 to 3, **characterized in that** the chelating agent used in the pretreatment step is chosen from N-carboxymethylaspartic acid, N-(1,2-dicarboxyethyl)-aspartic acid, N-(1,2-dicarboxy-2-hydroxyethyl aspartic acid, or compounds of formula:



where n is 1-3, m is 0-3, p is 1-3, R_1, R_2, R_3 and R_4 are H, Na, K, Ca or Mg, R_5 and R_6 are H, CH_2OH, CH_2CH_2OH or $CH_2O(CH_2CH_2O)_{1\text{-}10}CH_2CH_2OH$, and mixtures thereof.

5. Process according to claim 3, **characterized in that** the chelating agent is ethylenediamine-N,N'-disuccinic acid, its isomers and/or its salts, or 2,2'-iminodisuccinic acid, its isomers and/or its salts.

6. Process according to claims 1 to 5, **characterized in that** the initial pH of the pretreatment step is from 8,1 to 11.

7. Process according to claims 1 to 6, **characterized in that** the pretreatment step is carried out at a temperature from 40 to 95°C.

8. Process according to claims 1 to 7, **characterized in that** the pretreatment step is carried out in the presence of water in order to reach a consistency from 0.1 to 45% by weight of dry pulp.

9. Process according to claims 1 to 8, **characterized in that** the chelating agent used in the pretreatment step is used at a concentration from 0.1 to 1,5% by weight of dry pulp.

10. Process according to claims 1 to 9, **characterized in that** the oxidizing agent used in the bleaching step is chosen from hydrogen peroxide, organic peracids such as peracetic acid, or a combination thereof.

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EUROPEAN SEARCH REPORT

Application Number
EP 06 07 5155

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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	9 June 2006	Karlsson, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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