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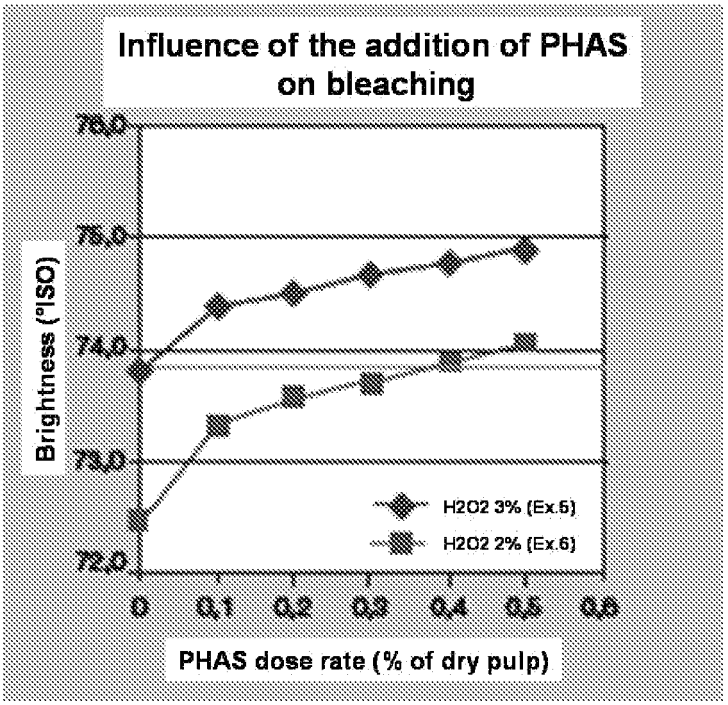
(54) Process for the bleaching of paper pulp

(57) Process for the bleaching of paper pulp in which an aqueous suspension of paper pulp is subjected to a bleaching treatment with hydrogen peroxide in the presence of magnesium hydroxide and of at least one poly-α-hydroxyacrylic acid, its salt or their mixture.

Figure 1



EP 2 128 331 A1

Description

[0001] The present invention relates to a process for the bleaching of paper pulp, especially mechanical paper pulp, through a bleaching treatment with hydrogen peroxide and an alkali source. Such bleaching treatment usually involves the use of peroxide stabilizers.

[0002] It is known to bleach mechanical paper pulp with oxidizing agents such as hydrogen peroxide in an alkaline medium and in the presence of a peroxide stabilizer.

[0003] For instance, the US patent 6221209 of SOLVAY INTEROX relates to a process for bleaching a chemical paper pulp by first purifying the pulp so as to reduce its manganese content and then by bleaching it with hydrogen peroxide in alkaline medium, especially at a pH adjusted to at least 10 by the addition of an alkaline compound (i.e. sodium hydroxide), and in the presence of a stabilizing agent, namely sodium silicate.

[0004] It is also known to use other alkaline sources than sodium hydroxide, such as magnesium hydroxide. For example, the US patent 7052578 discloses the use of magnesium hydroxide for the hydrogen peroxide bleaching of mechanical paper pulp.

[0005] However, even if, according to US 7052578, it is possible to reach high brightness results using magnesium hydroxide alone as alkaline source, it is more difficult compared to the use of sodium hydroxide and sodium silicate as it requires an extended reaction time, an increased peroxide charge, and the addition of chelating agents such as DTPA, even if a chelating step was conducted prior to the bleaching treatment.

[0006] When magnesium hydroxide is used as alkaline source in the hydrogen peroxide bleaching of mechanical paper pulp, it is difficult to achieve a satisfactory brightness, and the consumption of hydrogen peroxide for a given brightness is high.

[0007] The purpose of the present invention is to provide a process which does not present the above disadvantages and which enables to obtain a higher paper pulp brightness compared to the known use of other alkaline sources than sodium hydroxide, such as magnesium hydroxide or calcium hydroxide. The purpose of the present invention is also to provide a process which allows decreasing the consumption of hydrogen peroxide for a given brightness.

[0008] The present invention therefore relates to a process for the bleaching of paper pulp in which an aqueous suspension of paper pulp is subjected to a bleaching treatment with hydrogen peroxide in the presence of at least one alkaline earth hydroxide selected from magnesium hydroxide and calcium hydroxide and of at least one poly-α-hydroxyacrylic acid, its salt or their mixture.

[0009] Indeed, it has surprisingly been found that, in the presence of at least one poly-α-hydroxyacrylic acid, its salt or their mixture, it is possible to reach higher brightness, or to decrease the hydrogen peroxide consumption for a given brightness, when at least part of the alkaline compound is selected from alkaline earth hydroxides and especially from magnesium hydroxide and calcium hydroxide.

[0010] Furthermore, sodium silicate cannot be used when using alkaline earth hydroxides such as magnesium hydroxide and/or calcium hydroxide as alkaline source, because it forms precipitates with those products, leading to scaling. Such scaling creates problems in the whole production line including in the paper machine, when the mill is an integrated site. Thus, when alkaline earth hydroxides such as magnesium hydroxide and/or calcium hydroxide are used, the common practice is to bleach without any stabilizer, except aminopolycarboxylic acids or their salts, such as diethylene triamine penta-acetic acid (DTPA) or its sodium salt which will act as chelating agents and will therefore limit the decomposition of the hydrogen peroxide which is catalyzed by transition metals such as manganese or iron. Nevertheless, the conditions present during the bleaching are usually not suitable for a good efficiency of such chelating agents and therefore the effect of such stabilizers is very limited.

[0011] One of the essential features of the present invention resides in the combined use of an alkaline earth hydroxide selected from magnesium hydroxide and calcium hydroxide as alkaline source (referred to as "alkaline earth hydroxide according to the invention") and of poly-α-hydroxyacrylic acid, its salt or their mixtures (referred to as PHAA) as hydrogen peroxide stabilizer, during the hydrogen peroxide bleaching of paper pulp.

[0012] The PHAA used in the process of the invention generally has a molecular weight within a specific range. As the molecular weight is rather difficult to measure, it is inferred by measuring the viscosity, the higher the molecular weight, the higher the viscosity. Viscosity in the range of 10 to 100 mPa.s is usual but more particularly it can be in the range of 20 to 60 mPa.s. Commonly, the PHAA is used as a sodium salt of poly-α-hydroxyacrylic acid, corresponding to sodium poly-α-hydroxyacrylate (referred to as PHAS). In the invention, good results are obtained using only one PHAA. Nevertheless, more than one PHAA can be used.

[0013] The bleaching treatment according to the present invention is generally carried out at an initial pH of at least 8, in particular of at least 8,5, values of at least 9 being preferred. The initial pH is usually at most 14, in special cases at most 13, values of at most 12 being convenient. The pH of the aqueous suspension during the bleaching treatment is measured using equipment normally found in pulp mills for such a purpose. According to the invention, the natural pH of the paper pulp suspension is adjusted to the required value by means of an alkaline compound comprising at least one alkaline earth hydroxide selected from magnesium hydroxide and calcium hydroxide.

[0014] The amount of alkaline earth hydroxide according to the invention, used in the bleaching step of the present invention, is generally such that the pH of the suspension is maintained within the above-mentioned

range. This amount is usually at least 0,1 % by weight of dry pulp, preferably at least 1% by weight of dry pulp, more preferably at least 2% by weight of dry pulp. The amount of alkaline earth hydroxide according to the invention, used in the bleaching step of the present invention, is generally at most 10% by weight of dry pulp, with particular preference at most 5% by weight of dry pulp. The amount of alkaline earth hydroxide according to the invention, used in the bleaching step of the present invention, is for instance of from 2 to 5% by weight of dry pulp, for example about 3% by weight of dry pulp.

[0015] The amount of alkaline earth hydroxide according to the invention depends on the amount of hydrogen peroxide used and on the type of pulp. The ratio alkaline earth hydroxide according to the invention / hydrogen peroxide can for example vary from 0,3 to 2,5, preferably from 0,5 to 2,0 depending on the amount of hydrogen peroxide added and on the type of pulp. For example, the ratio may be about 1.

[0016] The alkaline earth hydroxide according to the invention is usually added to the paper pulp suspension in the form of an aqueous slurry. Preferably, the particle size of the alkaline earth hydroxide according to the invention is sufficiently small for the slurry to be readily suspendible, advantageously having a mean particle size of less than about 10 μm, preferably less than 6 μm, for example about 2 μm.

[0017] The bleaching step of the invention is generally carried out at a consistency of at least 10 % of dry pulp based on the weight of pulp suspension. The efficiency of the process increases as the consistency is increased up to a value of around 30 % by weight of dry pulp. The consistency can be up to 40 % by weight of dry pulp.

[0018] The bleaching treatment of the invention is usually carried out using an amount of hydrogen peroxide required to achieve the final target brightness. The amount of hydrogen peroxide is generally equal to or higher than 0,1 % by weight of dry pulp, preferably equal to or higher than 0,5 % by weight of dry pulp, more preferably equal to or higher than 1 % by weight of dry pulp. The amount of hydrogen peroxide is usually equal to or lower than 8 % by weight of dry pulp, especially equal to or lower than 6 % by weight of dry pulp, and more particularly equal to or lower than 5 % by weight of dry pulp. For example, the amount of hydrogen peroxide may be about 2 to 4% by weight of dry pulp.

[0019] The bleaching treatment of the invention is usually carried out at a temperature equal to or higher than 40°C, especially equal to or higher than 60°C. The temperature can be up to about 100°C. The temperature is preferably less than 100°C, more preferably equal to or less than 95°C, for example equal to or less than 85°C. The optimum bleach temperature depends on the wood type and pulping process but is normally in the range of 60 to 95°C.

[0020] The duration of the bleaching treatment of the process of the invention is usually from 10 min to 6 h, varying from mill to mill. For instance, it can vary from 30 to 300 min.

[0021] For example, the bleaching treatment can be carried out at a pH of from 8 to 14, at a consistency of from 10 to 40 %, and at a temperature of from 60 to 95°C, during 1 to 4 hours.

[0022] The amount of PHAA, especially PHAS, used in the bleaching step of the invention is usually equal to or higher than 0,05 % by weight of dry pulp, especially equal to or higher than 0,1 % by weight of dry pulp. The amount of PHAA is commonly equal to or lower than 2 % by weight of dry pulp, values of at most 1 % being suitable. For example, typical amounts of PHAA are about 0,1 to 0,5 % by weight of dry pulp. The optimum amount is dependent on the amount of metallic ions in the pulp and must be optimized for each particular mill.

[0023] The bleaching step of the invention can be carried out in the presence of any other alkaline or alkaline earth hydroxides than the alkaline earth hydroxides according to the invention, such as in the presence of sodium hydroxide. The bleaching step of the invention may also be carried out in the absence sodium hydroxide. The bleaching step of the invention can also be carried out in the presence of any other additives, such as magnesium sulfate or other soluble magnesium salts. Preferably, the bleaching step is carried out in the absence of any other stabilizer, and especially in the absence of sodium silicate.

[0024] In a preferred embodiment, prior to the bleaching treatment, the aqueous suspension of the paper pulp may be subjected to a chelating treatment to reduce the metallic ion content of the suspension, and especially its manganese content. It is for example usual to carry out a pretreatment step (or chelating treatment), with at least one aminopolycarboxylic acid, its salt or their mixture (referred to as APCA) prior to the bleaching treatment.

[0025] The APCA used in the pretreatment step is generally chosen from ethylene diamine tetra-acetic acid (EDTA), diethylene triamine penta-acetic acid (DTPA), triethylene tetramine hexa-acetic acid (TTHA), cyclohexane diamine tetra-acetic acid (CDTA), methylglycine diacetic acid (MGDA), nitrilo tri-acetic acid (NTA). The APCA may be used as the free acid, its salt or their mixtures. The APCA is preferably used as its salt. The salt is usually the alkali metal salt such as sodium or potassium or the ammonium salt or a mixture thereof. Sodium salts give good results. The most preferred APCA is the sodium salt of DTPA. Good results are generally obtained using only one APCA. Nevertheless, more than one APCA can be used. The chelating pretreatment step may be conducted as described in the International patent application filed as EP2008/052056, the text of which is incorporated herein by reference.

[0026] In a variant of the invention, the bleaching treatment may be carried out in the presence of at least one chelating agent, in particular of at least one APCA, such as those disclosed above. According to such a variant, the amount of APCA used in the bleaching treatment of the invention is usually at least 0,05 % wt based on the

weight of dry pulp. The amount of APCA is commonly at most about 1 % wt based on the weight of dry pulp, values of at most 0,8 % wt being suitable.

[0027] If at least one APCA is present during the bleaching treatment of the invention, the weight ratio between PHAA, especially PHAS, and APCA is usually at least 1:10, preferably at least 1:5, ratios of at least 1:3 being satisfactory. The weight ratio PHAA / APCA, especially PHAS / APCA, is generally at most 10:1, especially at most 5:1, values of at most 3:1 1 giving the best results.

[0028] In another variant of the invention, the bleaching treatment is carried out in the absence of a chelating agent or of another stabilizer than PHAA.

[0029] The paper pulp treated in the present invention can be chosen from chemical paper pulps, mechanical paper pulps or recycled paper pulps. The best results are obtained with mechanical paper pulps. 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 (CTMP) and alkaline peroxide mechanical pulp (APMP or APP). The present invention therefore also relates to the bleaching process of the invention applied to mechanical paper pulp.

[0030] The process of the invention can further comprise other treatment steps such as one or more additional dilution step(s), one or more additional chelating step(s), one or more additional bleaching step(s), one or more washing step(s) and/or one or more extraction step (s).

[0031] It is recommended to have a good mixing of the paper pulp to be treated with the hydrogen peroxide, the alkaline earth hydroxide according to the invention, and the PHAA. The order of addition of the alkaline earth hydroxide of the invention, the PHAA and the hydrogen peroxide is either first the PHAA, then the alkaline earth hydroxide of the invention, and lastly the hydrogen peroxide or first the alkaline earth hydroxide of the invention, then the PHAA, and lastly the hydrogen peroxide. Those three products may also be premixed all together or two of them can be premixed. The alkaline earth of the invention is usually added as a suspension in water. Dilution water may also be added. Usually, the reactants are introduced in the paper pulp suspension via a pump and a high consistency mixer, especially when the bleaching is performed at a consistency close to 30%. An example of configuration is : the chemicals are added in the preheating screw of the HC mixer.

[0032] The present invention is further illustrated below without limiting the scope thereto.

Examples 1 (comparative) and 2 (according to the invention

[0033] According to example 1, a mechanical pulp produced by a TMP process using spruce as raw material, at a consistency of about 15 %, was bleached at 80°C during 3 hours. Hydrogen peroxide was added in an amount of 3 % by weight of dry pulp. Magnesium hydroxide was added in an amount of 3 % by weight of dry pulp. The brightness of the paper pulp obtained in these conditions was 75,1°ISO and the residual peroxide content after the bleaching treatment was 9 % of the initial charge.

[0034] In example 2, the same conditions as in example 1 were applied except that 0,5% of PHAS were added to the bleaching step. The resulting brightness of the paper pulp was 76,6°ISO and the residual peroxide content was 17% of the initial charge.

[0035] Those two examples illustrate that, according to the invention, a higher brightness is obtained when a PHAA is added during the hydrogen peroxide bleaching of paper pulp in the presence of magnesium hydroxide as basic compound.

Examples 3 (comparative) and 4 (according to the invention)

[0036] In example 3, a mechanical pulp produced by a TMP process using spruce as raw material, at a consistency of about 15 %, was bleached at 70°C during 2 hours. Hydrogen peroxide was added in an amount of 3 % by weight of dry pulp. Magnesium hydroxide was added in an amount of 3 % by weight of dry pulp. The brightness of the paper pulp obtained in these conditions was 73,8°ISO and the residual peroxide content after the bleaching treatment was 27 % of the initial charge.

[0037] In example 4, the same mechanical pulp as in example 3 was bleached at 70°C during 2 hours in the presence of an amount of hydrogen peroxide of 2 % by weight of dry pulp, of magnesium hydroxide of 3 % by weight of dry pulp, and of an amount of PHAS of 0,3 % by weight of dry pulp. The resulting brightness of the paper pulp was the same as in example 3 (73,8°ISO) and the residual peroxide content was 31 % of the initial charge.

[0038] Those two examples illustrate that, according to the invention, it is possible to decrease the hydrogen peroxide consumption for a given brightness.

Examples 5 and 6 (Figure 1)

[0039] In example 5, a mechanical pulp produced by a TMP process using spruce as raw material, at a consistency of about 15 %, was bleached at 70°C during 2 hours. Hydrogen peroxide was added in an amount of 3 % by weight of dry pulp. Magnesium hydroxide was added in an amount of 3 % by weight of dry pulp. PHAS was added in an amount of 0 to 0,5 % by weight of dry pulp.

[0040] The same conditions as in example 5 were reproduced in example 6, except that the amount of hydrogen peroxide was 2 % by weight of dry pulp.

[0041] These results show that an amount of PHAS of 0,35 % by weight of dry pulp can reduce the hydrogen

peroxide consumption by 1 % by weight of dry pulp for the same brightness. These results also show that for an amount of hydrogen peroxide of 2 % by weight of dry pulp, the brightness of the resulting paper pulp can be increased from 72,4 to 73,9 °ISO by the addition of an amount of PHAS of 0,35 % by weight of dry pulp.

Claims

1. Process for the bleaching of paper pulp in which an aqueous suspension of paper pulp is subjected to a bleaching treatment with hydrogen peroxide in the presence of at least one alkaline earth hydroxide selected from magnesium hydroxide and calcium hydroxide and of at least one poly-α-hydroxyacrylic acid, its salt or their mixture.

2. Process according to claim 1, wherein the alkaline earth hydroxide is used in an amount of 0,1 to 10 % by weight of dry pulp.

3. Process according to claim 1 or 2, wherein the bleaching step is carried out in the absence of sodium hydroxide.

4. Process according to any one of claims 1 to 3, wherein the bleaching step is carried out in the absence of sodium silicate.

5. Process according to any one of claims 1 to 4, wherein, prior to the bleaching treatment, the aqueous suspension of the paper pulp is first subjected to a chelating treatment with at least one aminopolycarboxylic acid, its salt or their mixtures.

6. Process according to any one of claims 1 to 5, wherein the poly-α-hydroxyacrylic acid is in the form of its sodium salt.

7. Process according to any one of claims 1 to 6, wherein the bleaching treatment is carried out at a temperature equal to or less than 100°C, preferably of from 60 to 95°C.

8. Process according to any one of claims 1 to 7, wherein the bleaching step is carried out at an initial pH of from 8 to 14.

9. Process according to any one of claims 1 to 8, wherein the bleaching step is carried out at a consistency of from 10 to 40 %.

10. Process according to any one of claims 1 to 9, wherein the duration of the bleaching step is of from 1 to 6 hours.

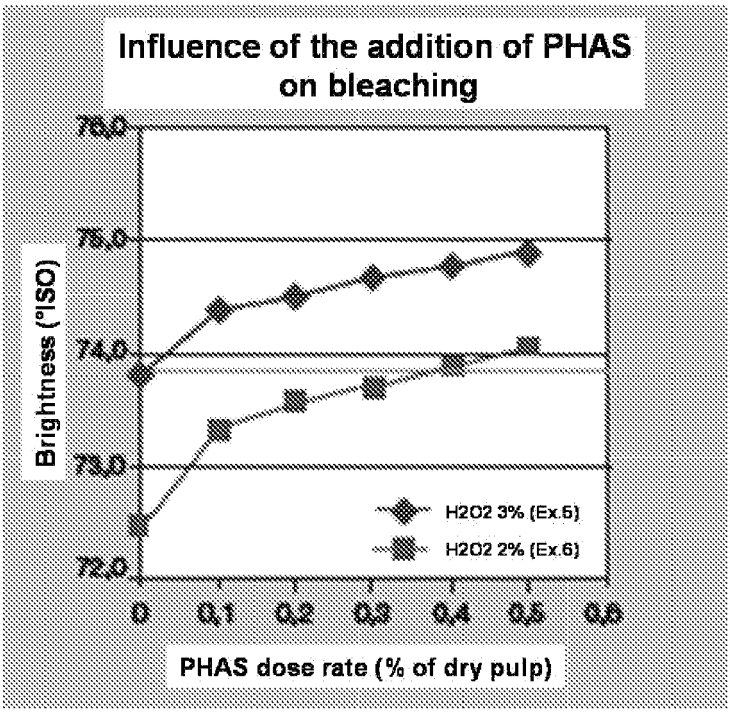
11. Process according to any one of claims 1 to 10, wherein the hydrogen peroxide is used in an amount of 0,1 to 8 % by weight of dry pulp.

12. Process according to any one of claims 1 to 11, wherein the poly-α-hydroxyacrylic acid, its salt or their mixture is used in an amount of from 0,1 to 2,0 % by weight of dry pulp.

13. Process according to any one of claims 2 to 12, wherein the aminopolycarboxylic acid, its salt or their mixture is chosen from the group consisting of ethylene diamine tetra-acetic acid, diethylene triamine penta-acetic acid, triethylene tetramine hexa-acetic acid, cyclohexane diamine tetra-acetic acid, methylglycine di-acetic acid, nitrilo tri-acetic acid, their salts, or mixtures thereof.

14. Process according to any one of claims 1 to 13 applied to the bleaching of mechanical paper pulp.

Figure 1


Influence of the addition of PHAS on bleaching
Brightness (°ISO)
76,0
76,0
74,0
72,0
0
0,1
0,2
0,3
0,4
0,5
0,6
PHAS dose rate (% of dry pulp)
H2O2 3% (Ex.6)
H2O2 2% (Ex.6)

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EUROPEAN SEARCH REPORT

Application Number
EP 08 15 6934

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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
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