PROCESS FOR THE BLEACHING OF PAPER PULP

Inventor: Rodney Seccombe, Hoeilaart (BE)

Correspondence Address:
Solvay
c/o B. Ortego - IAM-NAFTA
3333 Richmond Avenue
Houston, TX 77098-3099 (US)

Assignee: SOLVAY (SOCIETE ANONYME), Brussels (BE)

Appl. No.: 12/526,837
PCT Filed: Feb. 20, 2008
PCT No.: PCT/EP08/52056
§ 371 (c)(1), (2), (4) Date: Aug. 12, 2009

Foreign Application Priority Data
Feb. 21, 2007 (EP) 07102769.2

Publication Classification
Int. Cl. D21C 3/00 (2006.01)
U.S. Cl. 162/72

ABSTRACT

Process for the bleaching of paper pulp in which:

(a) an aqueous suspension of the paper pulp is first subjected to a chelating treatment with at least one aminopolyacrylic acid, its salt or their mixtures in order to reduce at least partially the metallic ion, especially manganese, content of the suspension, and

(b) the aqueous suspension of the paper pulp thus obtained is subjected to a bleaching treatment with hydrogen peroxide in the presence of

i. at least one poly-α-hydroxyacrylic acid, its salt or their mixtures, the function of which is to chelate at least partially iron present in the aqueous suspension, and

ii. at least one aminopolycarboxylic acid, its salt or their mixtures, the function of which is to chelate calcium present in the aqueous suspension thereby improving the performance of the poly-α-hydroxyacrylic acid, its salt or their mixtures.
PROCESS FOR THE BLEACHING OF PAPER PULP

[0001] The present patent application claims the benefit of the European patent application No. 07102769.2 filed on Feb. 21, 2007, herein incorporated by reference.

[0002] The present invention relates to a process for the bleaching of paper pulp, especially mechanical paper pulp, using a sequence of treatment steps, first a cleaning treatment followed by a bleaching treatment with hydrogen peroxide. Both treatments involve the use of additives such as poly-α-hydroxyacrylic acid or its salt or a mixture of both (referred to as PHAA) and a chelating agent of the aminopolycarboxylate type.

[0003] It is known to bleach mechanical paper pulp with oxidizing agents such as hydrogen peroxide. 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. Chelating agent may also be added during the bleaching step. Indeed, some metallic ions catalyze decomposition reactions of the peroxide compounds. The most detrimental ions are manganese, iron, and copper.

[0004] For instance, the U.S. Pat. No. 6,221,209 of SOLVAY INTEROX relates to a process for bleaching a chemically treated paper pulp by purifying first the pulp so as to reduce its manganese content and then by bleaching it with hydrogen peroxide in an alkaline medium in the presence of at least one chelating agent. This chelating agent is often necessary because the preliminary purification stage can not remove all the different types of metallic ions which are also favoring the decomposition of the hydrogen peroxide. For instance, diethylenetriamine-pentaacetic acid (DTPA) allows to chelate the manganese ions but not the iron ions. An example of a stabilizing agent is poly-α-hydroxyacrylic acid (called PHAA). PHAA is indeed an excellent non-silicate system for the replacement of water glass (sodium silicate) classically used in such a process. Indeed, water glass (sodium silicate) has severe drawbacks since the silicate can cause very severe precipitation problems. Another disadvantage with water glass is that, when the bleaching liquors from the mechanical pulping and bleaching operation are recycled and ultimately fed into the recovery boiler of a chemical pulp mill, where the so-called black liquor from the cooking process after concentration is burned, the silicate will cause severe scaling and thus decrease the heat transfer in the recovery boiler, which in worst case can cause an explosion of the recovery boiler. Furthermore, the use of sodium silicate can cause highly dusting.

[0005] The known process of the U.S. Pat. No. 6,221,209 presents still the following problem. Very often calcium is present in the water circuit of paper mills, coming from the wood, water hardness of the incoming raw process water or from calcium carbonate used as filler for the paper. As water circuits in mills become more closed to reduce the environmental impact, this becomes a more severe problem. So, in most cases calcium ions are present during the bleaching stage with hydrogen peroxide. It has been found that these calcium ions react with the stabilizer PHAA used during the H2O2 bleaching stage. A higher amount of stabilizer is thereby needed for preventing the decomposition of hydrogen peroxide. Furthermore, this causes scaling problems due to the precipitation of insoluble calcium compounds.

[0006] In the Japanese patent application JP 7010505, in the German patent application DE 3423452 and in the European patent application EP 0842321 the combined use of PHAA with diethylenetriamine-pentaacetic acid (DTPA) as additives in the bleaching of paper pulp with hydrogen peroxide is disclosed. However, none of these references discloses a preliminary chelating treatment step prior to the hydrogen peroxide bleaching treatment. In addition none of these references addresses the problem mentioned above.

[0007] The purpose of the present invention is to avoid the above-mentioned drawbacks by providing a new process for the bleaching of paper pulp which does not lead to scaling problems caused by insoluble calcium compounds, while lowering as much as possible the amount of stabilizing agent needed to avoid H2O2 decomposition.

[0008] The present invention therefore relates to a process for the bleaching of paper pulp in which:

[0009] (a) an aqueous suspension of the paper pulp is first subjected to bleaching treatment with at least one aminopolycarboxylic acid, its salt or their mixtures in order to reduce the metallic ion, especially manganese, content of the suspension,

[0010] (b) the aqueous suspension of the paper pulp thus obtained is subjected to a bleaching treatment with hydrogen peroxide and an alkali source in the presence of:

[0011] i. at least one poly-α-hydroxyacrylic acid, its salt or their mixtures (called PHAA), the function of which is to chelate at least partially iron present in the aqueous suspension, and

[0012] ii. at least one aminopolycarboxylic acid, its salt or their mixtures (called APCA), the function of which is to chelate calcium present in the aqueous suspension thereby improving the performance of the poly-α-hydroxyacrylic acid, its salt or their mixture.

[0013] One of the essential features of the present invention resides in the combined use of two additives in the hydrogen peroxide bleaching step, i.e. the combined use of PHAA and APCA, and especially the use of APCA in this step.

[0014] The combined use of PHAA and APCA results in an efficient stabilization of the hydrogen peroxide with a minimal amount of stabilizer PHAA needed. Indeed, it avoids that the stabilizer PHAA is consumed through a reaction with calcium, thereby also minimizing or avoiding that poorly soluble calcium compounds are formed which cause undesirable scaling problems.

[0015] The poly-α-hydroxyacrylic acid, its salt or their mixtures (referred to as 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.

[0016] The aminopolycarboxylic acid, its salt or their mixtures (referred to as APCA) used in the process of the invention is generally chosen from ethylene diamine tetra-acetic acid (EDTA), diethylenetriamine penta-acetic acid (DTPA), triethylene tetramine hexa-acetic acid (TTHA), cyclohexane diamine tetra-acetic acid (CDTA), methylglycine di-acetic acid (MGDA), nitro-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. In the invention, good results are obtained using only one APCA. Nevertheless, more than one APCA can be used.

[0017] Step (a) of the process of the present invention is usually carried out at a pH of at least 4, in particular of at least 4.5. The pH is generally at most 8, especially at most 7.5. pH values of from 4 to 8 give good results.

[0018] Step (a) of the process of the invention is generally carried out at a consistency of at least 1% of dry pulp. The consistency is commonly at most 40% of dry pulp. The consistency is highly variable depending on the point of addition in each mill.

[0019] Step (a) of the process of the present invention is generally carried out at a temperature of at least 40° C. The temperature is often at most about 100° C, preferably less than 100° C, more preferably equal to or less than 95° C, for example equal to or less than 85° C. The temperature is highly variable depending on the point of addition in each mill.

[0020] The amount of APCA used in step (a) of the process of the invention is generally at least 0.1% wt based on the weight of dry pulp. The amount of APCA is usually at most about 1% wt based on the weight of dry pulp. The optimum amount will vary from mill to mill depending on the wood source and metallic ion content.

[0021] The duration of step (a) of the process of the invention is usually fast requiring no more than a few minutes for the chelant to complex with the metallic ions but can be much longer, up to several hours, varying from mill to mill. The duration can range from about 5 min up to about 10 h.

[0022] For example, step (a) can be carried out at the natural pH of the pulp, ideally in the range of 4 to 8, using an amount of aminopolycarboxylic acid, its salt or their mixture of at least 0.1% by weight of dry pulp and at a temperature of at least 40° C.

[0023] Step (b) of the process of the present invention is generally carried out at a pH of at least 8, in particular of at least 8.5, values of at least 9 being preferred. The 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 treatment of step (b) is measured using equipment normally found in pulp mills for such a purpose. The pH of the suspension may be adjusted to the required value by means of pH modifying compounds. Such compounds may be selected from alkaline compounds because the natural pH of mechanical pulps is generally lower than the one required in practice. The alkaline compound is preferably sodium hydroxide.

[0024] Step (b) of the process of the present 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.

[0025] Step (b) of the process of the invention is carried out using an amount of hydrogen peroxide required to achieve the final target brightness. The amount is generally of at least 0.5% wt based on the weight of dry pulp. The amount of hydrogen peroxide is usually at most about 8% wt based on the weight of dry pulp.

[0026] The alkali source used in step (b) of the process of the invention is preferably sodium hydroxide. The amount used is such that the pH of the suspension is maintained within the above-mentioned range.

[0027] Step (b) of the process of the present 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 bleaching temperature depends on the wood type and pulping process but is normally in the range of 60 to 95° C. For example, step (b) 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.

[0028] The amount of PHAA, especially PHAS, used in step (b) of the process of the invention is usually at least 0.1% wt based on the weight of dry pulp. The amount of PHAA is commonly at most about 2% wt based on the weight of dry pulp values of at most 1% being suitable. The optimum amount is dependent on the amount of metallic ions in the pulp and must be optimized for each particular mill.

[0029] The amount of APCA used in step (b) of the process of the invention is 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.

[0030] The weight ratio between PHAA, especially PHAS, and APCA used in step (b) of the process of the invention 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 giving the best results.

[0031] The duration of step (b) 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.

[0032] Step (b) of the process of the invention can be carried out in the presence of other additives such as magnesium sulfate or other soluble magnesium salts.

[0033] Preferably, step (b) is carried out in the absence of any other stabilizer or chelating agent.

[0034] The paper pulp treated in the process of the 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), chemithermo-mechanical pulp (CTMP) and alkaline peroxide mechanical pulp (APMP or APP).

[0035] The process of the present invention leads to the following advantages:

[0036] A surprisingly identical or even higher brightness compared to a process wherein APCA is only used in step (a) and not in step (b) but with a higher amount of PHAA, especially PHAS, in step (b). Indeed, the addition of DTPA to a much lower level of PHAS than the optimum in step (b) can achieve similar brightness gains to that obtained with the optimum level of PHAS without the addition of APCA in step (b).

[0037] A surprisingly higher brightness of the paper pulp compared to a process wherein APCA is used in step (a) and PHAA, especially PHAS, in step (b) without using APCA in step (b), for levels of PHAA less than the optimum.

[0038] The process of the invention can further comprise other treatment steps such as 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).

[0039] It is recommended to have a good mixing of the paper pulp to be treated with the APCA and PHAS used in steps (a) and (b) of the process of the invention. This can be done by introducing them via a pump circulating the suspension of the pulp through the paper mill. The two chemicals (PHAA and APCA) can be pre-mixed prior to addition to the bleaching step (b) or added as a formulation in step (b). Alternatively, the two chemicals can be added separately to the bleaching step (b).

[0040] The present invention is further illustrated below without limiting the scope thereof.

Example 1

[0041] An integrated TMP mechanical pulp mill producing uncoated paper with an initial brightness of 58.1° ISO was pretreated with varying amounts of DTPA, diluted with water prior to thickening, then submitted to a bleaching process with hydrogen peroxide to determine the optimum level of DTPA required.

[0042] The pretreatment step was carried out at 60° C., during 30 minutes, at a consistency of 10% by weight of dry pulp and with a concentration of DTPA varying between 0 and 0.6%. Initial pH of the pretreatment step was that of the pulp at the point of addition. The pH was not adjusted after the addition of the chemicide agent, until the end of the pretreatment step.

[0043] 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 of around 25%. All the pretreated samples were then bleached as per the following conditions.

[0044] The bleaching step was carried out at 65° C., during 120 minutes and at a consistency of 15% by weight of dry pulp. H₂O₂ was added in an amount of 5% hydrogen peroxide based on the weight of dry pulp. NaOH was added in an amount of 4.2% based on the weight of dry pulp. 3.5% sodium silicate was added to the bleach liquor as stabilizer. From the bleaching results, the optimum level of DTPA was established as 0.25% for the pretreatment step. A large sample of pulp was then pretreated with 0.25% DTPA for subsequent bleaching studies.

[0045] The next step in the process was to optimize the level of PHAS added to the bleach liquor, which is dependent on the metallic ion content of the pulp.

[0046] The bleach liquor used was as above except that the sodium silicate was replaced with varying amounts of PHAS between 0 and 0.5%. The optimum level of PHAS at 0.35% gave a brightness increase of 19.0° ISO.

[0047] A level of PHAS of 0.1% was then chosen to which was added varying level of DTPA between 0 and 0.3% and again bleached as per the conditions above.

[0048] Brightness results are given in the table below.
1. A process for the bleaching of paper pulp comprising:
(a) first subjecting an aqueous suspension of the paper pulp to a chelating treatment with at least one aminopolycarboxylic acid, its salt or their mixtures in order to reduce at least partially the metallic ion content of the suspension, and
(b) subjecting the aqueous suspension of the paper pulp thus obtained to a bleaching treatment with hydrogen peroxide and an alkali source in the presence of
i. at least one poly-α-hydroxyacrylic acid, its salt or their mixtures, the function of which is to chelate at least partially iron present in the aqueous suspension, and
ii. at least one aminopolycarboxylic acid, its salt or their mixtures, the function of which is to chelate calcium present in the aqueous suspension thereby improving the performance of the poly-α-hydroxyacrylic acid, its salt or their mixtures.

2. The process according to claim 1, wherein the poly-α-hydroxyacrylic acid is in the form of its sodium salt.

3. The process according to claim 1, wherein step (b) is carried out at a temperature equal to or less than 100°C.

4. The process according to claim 1, wherein step (a) is carried out at the natural pH of the pulp in the range of 4 to 8 using an amount of aminopolycarboxylic acid, its salt or their mixture of at least 0.1% by weight of dry pulp and at a temperature of at least 40°C.

5. The process according to claim 1, wherein step (b) is carried out at a pH of from 8 to 14, at a consistency of from 10 to 40% of dry pulp based on the weight of pulp suspension, and at a temperature of from 60 to 95°C.

6. The process according to claim 1, wherein step (b) is carried out by using an amount of poly-α-hydroxyacrylic acid, its salt or their mixture of from 0.1 to 2.0 wt-% based on the weight of dry pulp, and an amount of aminopolycarboxylic acid, its salt or their mixtures of from 0.05 to 1.0 wt-% based on the weight of dry pulp.

7. The process according to claim 1, wherein, in step (b), the weight ratio between the poly-α-hydroxyacrylic acid, its salt or their mixture and the aminopolycarboxylic acid, its salt or their mixture is of from 1:10 to 10:1.

8. The process according to claim 1, wherein the aminopolycarboxylic acid, its salt or their mixture is selected from the group consisting of ethylene diamine tetra-acetic acid, diethylenetriamine penta-acetic acid, triethylene tetramine hexaacetic acid, cyclohexane diamine tetra-acetic acid, methylglycine di-acetic acid, nitrilo tri-acetic acid, their salts, and mixtures thereof.
9. The process according to claim 1, wherein the aminocarboxylic acid used in steps (a) and (b) is diethylenetriamine penta-acetic acid or its sodium salt.

10. The process according to claim 1, wherein step (b) is carried out in the absence of any other stabilizer or chelating agent.

11. The process according to claim 1 which is applied to the bleaching of mechanical paper pulp.

12. The process according to claim 1, wherein step (a) is carried out in order to at least partially reduce the manganese content of the suspension.

* * * * *