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(54) **Method for removing unsaturated uronic acid in chemical pulp for papermaking**

(57) The present invention provides a method for removing unsaturated uronic acid contained in chemical pulp for papermaking, characterized by adding glucuronidase. According to the preferred embodiment of the present invention, in an ECF or TCF bleaching method

using no molecular chlorine, unsaturated uronic acid can be reduced while controlling a bleaching cost, and a brightness reversion property of pulp can be improved.

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DescriptionTECHNICAL FIELD

- 5 **[0001]** The present invention relates to treatment of chemical pulp for papermaking, more specifically to a method for removing unsaturated uronic acid contained in chemical pulp.

BACKGROUND ART

- 10 **[0002]** Bleaching of chemical pulp for papermaking is carried out by bleaching treatment through a multistage. Chlorine base bleaching chemicals as a bleaching agent have so far been used for this multistage bleaching. To be specific, bleaching has so far been carried out by the sequences of, for example, C-E-H-D and C/D-E-H-E-D (C/D is a bleaching stage by combined use of chlorine and chlorine dioxide; E is an alkali extracting stage; and - is washing treatment) in the combination of chlorine (C), hypochlorite (H) and chlorine dioxide (D).
- 15 **[0003]** However, these chlorine base bleaching chemicals by-produce organic chlorine compounds which are harmful to the environment in bleaching, and environmental pollution caused by bleaching waste water containing these organic chlorine compounds brings about problems. In general, organic chlorine compounds are analyzed and evaluated by an AOX method, for example, U.S. Environment Agency (EPA, METHOD-No. 9020).
- 20 **[0004]** It is the most effective for reducing or preventing by-production of organic chlorine compounds that a dosage of chlorine base bleaching chemicals is reduced or they are not used. In particular, it is the most effective method that molecular chlorine is not used in the first stage. Pulp produced by this process is called ECF (elementary chlorine free) bleached pulp. Further, pulp which is produced without using chlorine base bleaching chemicals is called TCF (totally chlorine free) bleached pulp.
- 25 **[0005]** Bleaching by a D-Eo-D or D-Eo-D-D sequence in which chlorine dioxide is used in the first stage and a D-Eop-D, D-Eop-P-D or D-Eo-P-D sequence in which hydrogen peroxide is used in an alkali stage are usually known as a method in which pulp subjected to cooking-oxygen delignification treatment is bleached without using molecular chlorine in the first stage (Chlorine Dioxide in Delignification, Pulp & Paper, University of Toronto). In this case, Eo is an alkali extracting stage in which oxygen is added; Eop is an alkali extracting stage in which oxygen and hydrogen peroxide are added; and P is a hydrogen peroxide bleaching stage.
- 30 **[0006]** However, chlorine dioxide has a low ability for removing hexeneuronic acid (hereinafter referred to as HexA) as compared with that of chlorine which has so far been used, and therefore a large amount of HexA remains in pulp after bleaching. This remaining HexA causes a deterioration in a brightness stability (brightness reversion property) of ECF or TCF bleached pulp (Tappi Journal May 2003, vol. 2, No. 5).
- 35 **[0007]** HexA is a substance produced by allowing methanol to be eliminated in a cooking step from an end of glucuronic acid bonded to xylan which is hemicellulose present in pulp. Less effect is exerted on a brightness of pulp, but it is counted as a K value or a Kappa value by reacting with potassium permanganate since it has a double bond in a molecule (Tappi Journal May 2003, vol. 2, No. 5).
- 40 **[0008]** A method in which a dosage of chlorine dioxide or ozone is increased to remove HexA in order to improve the above deterioration in a brightness reversion property is available. However, an increase in a dosage of these oxidizing agents which are expensive as compared with conventional chlorine brings about the problem that the bleaching cost grows high to a large extent since HexA consumes these oxidizing agents by virtue of double bonds in molecules.
- 45 **[0009]** A method for removing HexA by acid treatment at high temperature is disclosed in Papehi ja Puu-Paper and Timber, Vol. 86, No. 1, 2004. A method for removing HexA by acid hydrolysis in acid treatment on the condition of 90°C for 180 minutes at a pH of 3 is proposed. This method makes it possible to remove HexA only by controlling pH by inexpensive acid, and therefore it is an effective method. However, a large amount of vapor is required, and therefore the bleaching cost unavoidably grows large as well. Also, if the treating temperature is controlled to about 70°C in order to cut the vapor cost, HexA is scarcely removed. Further, brought about is the problem that acid treatment at high temperature requires an expensive material such as Hastelloy which is durable to corrosion as an apparatus material in order to carry out acid treatment at high temperature.
- 50 **[0010]** Further, a method for removing HexA by strengthening a chlorine dioxide-treating condition is disclosed in Papehi ja Puu-Paper and Timber, Vol. 86, No. 1, 2004. That is, it is a method for removing HexA by treatment at a bleaching temperature of 90°C and a pH of 3 for a treating time of 120 to 180 minutes. The above method is a method in which acid treatment at high temperature is combined with chlorine dioxide treatment. This method has the problems that a large amount of vapor is required as is the case with the acid treatment and that it is inferior in a rise in the
- 55 brightness as compared with conventional chlorine dioxide treatment since chlorine dioxide treatment is carried out at high temperature. Further, there is the problem that an expensive material is required to the apparatus material since the treatment is carried out at high temperature.
- [0011]** It is reported in Research Report of Forestry and Forest Products Research Institute, No. 359, p. 141 to 157

to search microorganisms producing α -(1 $\rightarrow$ 2)-glucuronidase which liberates 4-O-methyl-D-glucuronic acid from hard wood xylan. This research has a purpose of removing 4-O-methyl-D-glucuronic acid (saturated uronic acid) by α -glucuronidase to saccharify hard wood xylan. The present inventors have a purpose of removing hexeneuronic acid (unsaturated uronic acid) bonded to xylan contained in hard wood pulp which is bleached by oxygen after cooking treatment, and suggestions on the present invention are not disclosed at all in the report.

[0012] A method in which pulp is treated by a bleaching enzyme and in which the enzyme is recovered and reused is described in Japanese Unexamined Patent Publication No. 1993-247865. It is described that hemicellulase is used as one of bleaching enzymes, and glucuronidase is described therein as the example of the hemicellulase. However, removal of unsaturated uronic acid by adding glucuronidase which is the method of the present invention is not disclosed therein at all.

[0013] Investigations of glucuronidase are described in Research Report of Forestry and Forest Products Research Institute, No. 359, p. 141 to 157 and Japanese Unexamined Patent Publication No. 1993-247865, but the above enzyme is usually used for removing saturated uronic acid. Accordingly, it is surprising that α -glucuronidase can remove unsaturated uronic acid as found in the present invention, and it is not described in the prior documents described above to suggest it.

DISCLOSURE OF INVENTION

[0014] An object of the present invention is to provide a method in which in producing chemical pulp for papermaking, an increase in a bleaching cost is minimized in ECF bleaching or TCF bleaching using no molecular chlorine in the first stage and in which HexA remaining in the pulp is removed while maintaining a pulp viscosity.

[0015] Intensive investigations repeated by the present inventors on enzyme treatment of pulp subjected to cooking-oxygen delignification treatment have resulted in finding that glucuronidase obtained by cultivating basidiomycete and/or filamentous fungus as microorganisms can remove HexA remaining in pulp while maintaining a pulp viscosity, and thus they have completed the present invention. That is, the present invention relates to a method for removing unsaturated uronic acid contained in chemical pulp for papermaking, characterized by adding glucuronidase. In this case, α -glucuronidase is preferred for glucuronidase.

[0016] The present invention relates to a method for removing unsaturated uronic acid, which is described below in more details.

(1) A method for removing unsaturated uronic acid contained in chemical pulp for papermaking, characterized by adding glucuronidase.

(2) The method as described in the item (1), wherein glucuronidase contains xylosidase or xylanase.

(3) The method as described in the item (1) or (2), wherein glucuronidase contains α -glucuronidase.

(4) The method as described in any of the items (1) to (3), wherein unsaturated uronic acid is hexeneuronic acid.

(5) The method as described in any of the items (1) to (4), wherein glucuronidase is produced from basidiomycete or filamentous fungus.

(6) The method as described in any of the items (2) to (4), wherein xylosidase or xylanase is produced from basidiomycete or filamentous fungus.

(7) The method as described in the item (5) or (6), wherein the basidiomycete is a *Cholorosplenium* genus.

(8) The method as described in the item (5) or (6), wherein the filamentous fungus is an *Aspergillus* genus.

(9) The method as described in the item (7), wherein the *Cholorosplenium* genus is *Cholorosplenium aeruginosum*.

(10) The method as described in the item (8), wherein the *Aspergillus* genus is *Aspergillus niger*.

(11) The method as described in any of the items (5) to (10), wherein glucuronidase, xylosidase or xylanase is produced on a culture medium containing xylan.

(12) The method as described in any of the items (5) to (11), wherein glucuronidase produced is added to the pulp without refining.

(13) The method as described in any of the items (1) to (12), wherein glucuronidase is added to the pulp after oxygen treatment, during a bleaching treating step or after bleaching treatment.

(14) The method as described in the item (13), wherein the pulp is ECF bleached pulp or TCF bleached pulp.

[0017] According to the present invention, it becomes possible, though there has been the problem that a brightness reversion property of finished bleached pulp in non-chlorine bleaching carried out mainly by chlorine dioxide is deteriorated, to remove HexA contained in pulp at temperature of a conventional bleaching step without increasing the amounts of expensive chlorine dioxide and ozone and requiring additionally heating. According to the preferred embodiment of the present invention, a heat induced brightness reversion property of pulp produced by an ECF or TCF bleaching method in which molecular chlorine is not used can be improved while maintaining excellent pulp physical properties and controlling a bleaching cost to a lower level.

BEST MODE FOR CARRYING OUT THE INVENTION

[0018] The pulp treated in the present invention is preferably pulp originating in a chemical pulping method such as a conventional kraft pulping method (KP) including a polysulfide method (PS), a sulfite pulping method (SP) and an alkali pulping method (AP), more preferably pulp obtained by the kraft pulping method. Arboreous plants and herbaceous plants used for pulping shall not specifically be restricted. Pulp to be treated is subjected to publicly known oxygen delignification treatment as pre-treatment so that a Kappa value becomes 20 or less, and it is preferably pulp having a Kappa value of 12 or less.

[0019] Glucuronidase or glucuronidase containing xylosidase or xylanase used in the present invention is produced from basidiomycetes or filamentous fungus. The basidiomycetes include a *Chlorosplenium* genus such as *Agrocybe cylindracea*, *Anellaria semiovata*, *Astereophora lycoperdoides*, *Auricularia auricular-judae*, *Auriscalpium vulgare*, *Bondarezewia montana* and *Chlorosplenium aeruginosum*, *Clitocybe acromelalga*, *Clitocybe nebularis*, *Coriolus consors*, *Coriolus hirsutus*, *Coriolus pubescens*, *Coriolus versicolor*, *Cortinarius cinnamomeus*, *Crinipellis stipitaria*, *Cryptoporus volvatus*, *Cyathus stercoreus*, *Cyclomyces fuscus*, *Cymatoderma elegans*, *Daedaleopsis tricolor*, *Daldinia concentrica*, *Favolus arcularius*, *Filoboletus manipularis*, *Flammulina velutipes*, *Formes formentarius*, *Fomitopsis pinicola*, *Hebeloma radicosum*, *Hirschioporus abietinus*, *Inonotus cuticularis*, *Irpex lacteus*, *Lactarius chrisorheus*, *Laetiporus sulphureus*, *Lampteromyces japonicus*, *Lentinus edodes*, *Lentinus lepideus*, *Lenzites betulina*, *Lepista nuda*, *Lyophyllum shmeji*, *Macrolepiota procera*, *Merunius tremellosus*, *Naematoloma sublateritium*, *Onnia orientalis*, *Oudemansiella mucida*, *Oudemansiella radicata*, *Penellus serotinus*, *Panus rudis*, *Phanerochaete chrysosporium*, *Pholiota adiposa*, *Pholiota aurivella*, *Pholiota nameko*, *Pleurotus ostreatus*, *Podostroma cornu-damae*, *Polyporellus brumalis*, *Polyporellus tuberaster*, *Porodiscus pendulus*, *Pseudohiatula ohshimase*, *Psilocybe argentipes*, *Pycnoporus coccineus*, *Schizophyllum commune*, *Stereum annosum*, *Stereum frustulosum*, *Stereum hirsutum*, *Stereum roseum*, *Stropharia aeruginosa*, *Trametes albida*, *Trametes gibbosa*, *Tremella foliacea*, *Tremella fuciformis*, *Urnula craterium* and *wynnea gigantea*. Among them, the *Chlorosplenium* genus is preferred, and *Chlorosplenium aeruginosum* is particularly suited.

[0020] The mould fungi include an *Aspergillus* genus such as *Aspergillus niger*, *Aspergillus japonicus*, *Aspergillus pulverulentus*, *Aspergillus terreus* and *Aspergillus versicolor* and a *Trichoderma* genus such as *Trichoderma aureoviride*, *Trichoderma hamatum*, *Trichoderma harzianum*, *Trichoderma koningii*, *Trichoderma longibrachitum*, *Trichoderma viride* and *Trichoderma reesei*. Among them, the *Aspergillus* genus is preferred, and *Aspergillus niger* is particularly suited.

[0021] Crude glucuronidase which is not refined after produced from basidiomycetes or mould fungi can be used as well.

[0022] Further, a mixture obtained by adding glucuronidase to a xylan-degrading enzyme such as xylosidase and xylanase can be used as well. A substance discharged by a snail can also be used as glucuronidase.

[0023] When using, for example, *Aspergillus niger* as production microorganism, it is cultivated at 35°C for 24 hours in a liquid culture medium containing 2 % xylan. This cultivated liquid is filtered, and a fungus body obtained is crushed and then extracted with a 0.1M acetic acid buffer solution (pH 5) to obtain a glucuronidase-containing crude enzyme. Then, this enzyme is refined by ion exchange chromatography and gel chromatography to obtain glucuronidase. Crude enzyme which is not refined may be used as glucuronidase.

[0024] The enzyme treatment carried out in the present invention is preferably carried out under the treating conditions of a treating pH of 2.0 to 7.0 and a treating time of 1 to 12 hours in a dosage of glucuronidase of 4 to 40,000 units per g of the pulp. A treating temperature of 30 to 90°C and a pulp consistency of 3 to 30 % are preferred. The pulp consistency shows a proportion of a pulp weight in a treating solution containing the pulp, an enzyme treating liquid and water. Glucuronidase is added to non-bleached pulp after oxygen bleaching, an intermediate part between various ECF or TCF bleaching stages and after finishing bleaching, but a position for adding glucuronidase may be any one as long as it agrees with the treating conditions of glucuronidase.

[0025] After enzyme treatment, the pulp is sent to an ECF or TCF bleaching sequence which is a subsequent stage without washing or after washing. The washing treatment shall not specifically be restricted as long as it is usually used in bleaching treatment of chemical pulp for papermaking.

[0026] A bleaching sequence in which molecular chlorine is not used includes ECF sequences in which chlorine dioxide is mainly used, such as D-Ep-D, D-Eop-D, D-Ep-P-D, D-Eop-P-D, D-Ep-D-D, D-Eop-D-D, D-Ep-D-P and D-Eop-D-P. Also, it includes ECF sequences in which ozone is mainly used, such as Z-Ep-D, Z-Eop-D, Z-Ep-P-D, Z-Eop-P-D, Z-Ep-D-D, Z-Eop-D-D and Z-Ep-D-P and ECF sequences in which ozone and chlorine dioxide are used in combination, such as Z/D-Ep-D, Z/D-Eop-D, Z/D-Ep-P-D, Z/D-Eop-P-D, Z/D-Ep-D-D, Z/D-Eop-D-D, Z/D-Ep-D-P and Z/D-Eop-D-P. Further, it includes TCF sequences such as Z-Ep-P, Z-Eop-P, Z-Ep-P-P, Z-Eop-P-P, Z-Ep-Q-P and Z-Eop-Q-P. In this case, Ep is an alkali extracting stage in which hydrogen peroxide is added; Q is a chelating agent-adding treating stage; Z is an ozone bleaching stage; and Z/D is a bleaching stage in which ozone and chlorine dioxide are used in combination. The above bleaching sequences shall by no means restrict the present invention. In this case, glucuronidase may be added to such addition positions as intermediate stages of the bleaching sequences described above and the finished pulp after finishing bleaching. The addition position may be a single position or plural positions.

[0027] In the present invention, a brightness reversion property of ECF bleached or TCF bleached pulp can be improved

by treating pulp with the enzyme. The first characteristic of the method of the present invention is that a selectivity in an enzyme reaction is very high to remove only HexA which is a problem for a brightness reversion property, so that excellent pulp can be produced without entirely exerting an effect on the physical properties of the pulp.

[0028] An oxidizing agent such as ozone and chlorine dioxide not only removes HexA but also removes lignin and saccharides in pulp to excess, and therefore not only the physical properties such as a viscosity of the pulp are reduced, but also brought about is the problem that COD of the waste water is increased, which is not preferred in terms of the environment. Thus, the second characteristic of the present invention is that use of the enzyme in the method of the present invention makes it possible to produce the pulp with scarcely bringing about such problems.

[0029] A large amount of energy is required for producing chlorine dioxide and ozone, and the third characteristic of the present invention is that the enzyme used in the present invention is produced by microorganisms and therefore can be produced in a very small amount of energy.

[0030] That is, the characteristic of the present invention is that introduction of the enzyme treatment using glucuronidase into a conventional ECF bleaching or TCF bleaching sequence makes it possible to remove HexA while maintaining a viscosity of the pulp in low temperature treatment of 40 to 70°C in which removal of HexA has so far been assumed to be difficult. Further, the characteristic of the present invention is that substances other than HexA are less damaged, so that the method of the present invention can be carried out without raising COD of the waste water. The method of the present invention makes it possible to provide a production process for bleached pulp in which chemicals are controlled in use to the utmost by making use of the enzyme, and therefore it is a production method for pulp which is very excellent in terms of the environment.

EXAMPLES

[0031] Next, the present invention shall specifically be explained with reference to examples. The examples shown below are exhibited in order to specifically explain the present invention, and the present invention shall by no means be restricted by them.

1. Preparation of substrate

[0032] A hard wood oxygen bleached kraft pulp (LOKP) 30 g having a Kappa value of 10 was treated with cellulase [Onozuka] 3S. The pulp consistency was controlled to 5 %. A soluble part (saccharified liquid) obtained was subjected to activated carbon treatment by a batch system to adsorb the enzyme, colored substances and products having a large molecular weight on the activated carbon, and the activated carbon was filtered off to remove them. The filtrate was allowed to flow in a column charged with activated carbon. Water was allowed to flow in the column to elute inorganic salts and monosaccharides. Next, a 40 % ethyl alcohol-60 % water mixed solution was allowed to flow therein to elute oligosaccharide. The oligosaccharide 5.3 g was obtained from the saccharified liquid 600 g. Acid sugars and neutral sugars were contained in the oligosaccharide.

[0033] An anionic ion exchange resin (Dowex IX2) was equilibrated by a 0.1M acetic acid aqueous solution and converted to an acetic acid type, and it was charged into a column. On the other hand, an aqueous solution of oligosaccharide was controlled to pH 8 to 9 by NaOH and left standing for one hour to open a lactone ring. This was allowed to flow in the column. A 0.1M acetic acid aqueous solution was allowed to flow in the column to elute neutral sugars. Next, a 2M acetic acid aqueous solution was allowed to flow therein to elute acid sugars. The acid sugar solution was neutralized with NaOH and subjected to electrodialysis, and then it was lyophilized. The principal component of the lyophilized sample was an acid sugar oligomer (Δ -X4) of a pentamer in which one hexeneuronic acid (Δ) was bonded to xylose tetramer (X4).

2. Preparation of enzyme solution

[0034] Six kinds of microorganisms were used to prepare the enzyme. *Irpex lacteus*, *Chlorosplenium aeruginosum*, *Merulius tremellosus*, *Coriolus pubescens* and *Coriolus versicolor* were subjected to liquid cultivation at 25°C for 7 days in a liquid culture medium comprising 1 % hard wood xylan as a carbon source, and *Aspergillus niger* was cultivated at 35°C for 24 hours on a culture medium containing 2 % xylan. The respective culture solutions were filtered, and using the filtrates as extracellular enzymes, the fungus bodies thus obtained were crushed and then extracted with a 0.1M acetic acid buffer solution (pH 5.0). This enzyme was used as a crude enzyme. α -Glucuronidase, β -xylosidase and β -xylanase were contained in this enzyme. Refined α -glucuronidase was obtained from the above crude enzyme by ion exchange chromatography and gel chromatography.

3. Analytical method

[0035] The enzyme reaction product was analyzed by a fluorescent labeling electrophoresis (FACE) of sugar.

[Examples 1 and 2]

[0036] An acetic acid buffer solution 20 μ l of pH 5 and an intracellular enzyme solution 30 μ l were added to a 2 mM solution 50 μ l of Δ -X4 taken out from LOKP, and they were reacted at 40°C for 24 hours. The enzyme reaction product was analyzed by the fluorescent labeling electrophoresis (FACE) of sugar.

[0037] The crude enzyme produced by *Aspergillus niger* and *Chlorosplenium aeruginosum* showed an activity to Δ -X4. The results thereof are shown in Table 1.

[Comparative Examples 1 and 4]

[0038] A crude enzyme produced from *Irpex lacteus*, *Coriolus pubescens*, *Coriolus versicolor* and *Merulius tremellosus* in place of the microorganisms used in Examples 1 and 2 was reacted with Δ -X4 taken out from LOKP in the same manner. The results thereof are shown in Table 1.

Table 1

	Microorganisms	Judgment
Example 1	<i>Aspergillus niger</i>	+
Example 2	<i>Chlorosplenium aeruginosum</i>	+
Comparative Examples 1	<i>Irpex lacteus</i>	-
Comparative Examples 2	<i>Coriolus pubescens</i>	-
Comparative Examples 3	<i>Coriolus versicolor</i>	-
Comparative Examples 4	<i>Aferulius tremellosus</i>	-

A force of each enzyme for cutting a bonding part of xylose tetramer and one hexeneuronic acid(Δ -X4)

+: cut -:not cut

[0039] That is, the intracellular enzymes of *Aspergillus niger* and *Chlorosplenium aeruginosum* could cut the bonding part of a xylose tetramer and one hexeneuronic acid (Δ -X4) and remove hexeneuronic acid. As a result thereof, xylose tetramer (X4) was produced. The bond of X4 was readily cut by β -xylosidase and β -xylanase to produce xylose. The intracellular enzymes of *Irpex lacteus*, *Coriolus pubescens*, *Coriolus versicolor* and *Merulius tremellosus* could not cut the bonding part of the xylose tetramer and one hexeneuronic acid.

[Examples 3 to 5]

[0040] Next, the examples of hard wood pulp shall be described. The dosage of the respective chemicals are shown by weight % based on bone dried pulp, and a dosage of hydrogen peroxide is reduced to 100 %. Hard wood pulp A after kraft cooking-oxygen delignification was used for the pulp. Analysis and evaluation were carried out by the following methods.

Pulp kind:

A; brightness by Hunter: 50.1 %, K value: 6.64, viscosity: 28.9 mPa·s, HexA: 39.8 μ mol/g

· Brightness: JIS-P8123 (brightness-by-Hunter method)

· K value: TAPPI K value method

· Viscosity: J. TAPPI No. 44 method

· HexA amount: pulp of an bone dried amount of 1 g was diluted to a pulp consistency 1 % and controlled to pH 3.0 by formic acid, and then it was heated at 90°C for 240 minutes to hydrolyze HexA to 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid. After cooled, the pulp was separated from water. The amounts of 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid contained in water were determined by liquid chromatography using a detector of UV 265 nm, and the total amount thereof was set as an amount of HexA.

· Brightness reversion test: 85°C - 65 % RH, 24 hours

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·PC value: measure for the grade of the brightness reversion degree

PC = 100 (K/S after brightness reversion - K/S before brightness reversion)

K/S = (1-brightness)²/(2 brightness)

[0041] The crude enzyme produced by *Aspergillus niger* was added to 20 g of hard wood pulp A after kraft cooking-oxygen delignification in 10 units, 20 units and 30 units, and the mixture was treated for 180 minutes on the conditions of a pulp consistency of 10 %, a pH of 5 and a temperature of 40°C. After finishing the reaction, it was diluted to a pulp consistency of 2.5 % with cold water and dehydrated up to a pulp concentration of 20 % to obtain enzyme-treated pulp. The results thereof are shown in Table 2.

[Example 6]

[0042] The same procedure as in Example 3 was carried out, except that 20 units of α -glucuronidase separately refined was added to the crude enzyme produced by *Aspergillus niger*. The results thereof are shown in Table 2.

[Comparative Example 5]

[0043] The same treatment as in Example 3 was carried out, except that the enzyme was not added in Example 3. The results thereof are shown in Table 2.

Table 2

	Enzyme (unit)	HexA amount (μ mol/g)
Comparative Examples 5	No addition	39.3
Examples 3	10	34.7
Examples 4	20	29.3
Examples 5	30	24.2
Examples 6	30	13.1

[0044] That is, HexA could be removed by adding the enzyme of the present invention to non-bleached pulp. Further, as shown in Example 6, α -glucuronidase obtained by refining an enzyme produced by *Aspergillus niger* was added to the crude enzyme used in Examples 3, and the mixture was used to find that HexA could be removed to a large extent in the same enzyme unit.

[Example 7]

[0045] The pulp A subjected to oxygen bleaching after kraft cooking was used to carry out bleaching by a bleaching sequence of G-D-Eop-D in which enzyme bleaching was introduced into the first stage. The crude enzyme produced by *Aspergillus niger* was used for the enzyme.

G (enzyme treatment): PC 10 %, pH 5, 40°C, 180 minutes, enzyme: 100 units

First stage D: PC 10 %, 60°C, 30 minutes, ClO₂/0.9 %

Eop: PC 10 %, 60°C, 90 minutes, NaOH/0.8 %, O₂/0.15 %, H₂O₂: 0.3 %

D: PC 10 %, 70°C, 120 minutes, ClO₂/0.4 %

Washing condition: after finishing the reactions at the respective stages, the pulp was diluted to a pulp consistency of 2.5 %, and it was dehydrated to a pulp consistency of 20 % and transferred to a subsequent stage. The results thereof are shown in Table 3.

[Example 8]

[0046] The same procedure as in Example 7 was carried out, except that enzyme treatment was introduced into the middle of a bleaching stage in a bleaching sequence of D-Eop-G-D. The results thereof are shown in Table 3.

[Example 9]

[0047] The same procedure as in Example 7 was carried out, except that enzyme treatment was introduced into the final stage of a bleaching stage in a bleaching sequence of D-Eop-D-G. The results thereof are shown in Table 3.

[Comparative Example 6]

[0048] The same procedure as in Example 7 was carried out, except that the enzyme treatment was not carried out. The results thereof are shown in Table 3.

Table 3

	Brightness (%)	Kappa value	HexA amount ($\mu\text{mol/g}$)	PC value
Example 7	86.4	1.2	2.5	1.9
Example 8	87.2	0.7	2.3	1.7
Example 9	88.1	0.9	1.2	1.4
Comparative Examples 6	85.7	2.7	13.6	4.6

[0049] That is, the brightness reversion degree which was a problem in the finished pulp could be improved by introducing the enzyme treatment into the bleaching sequence in which chlorine dioxide and hydrogen peroxide were used.

[Example 10]

[0050] The pulp A subjected to oxygen bleaching after kraft cooking was used to carry out bleaching by a bleaching sequence of G-Z-E-P in which enzyme bleaching was introduced into the first stage. The enzyme produced by *Aspergillus niger* was used for the enzyme.

G (enzyme treatment): PC 10 %, pH 5, 40°C, 180 minutes, enzyme: 100 units

First stage Z: PC 10 %, 60°C, 3 minutes, $\text{O}_3/0.5$ %

E: PC 10 %, 60°C, 90 minutes, NaOH/0.8 %

P: PC 10 %, 90°C, 120 minutes, $\text{H}_2\text{O}_2/1.5$ %

Washing condition: after finishing the reactions at the respective stages, the pulp was diluted to a pulp consistency of 2.5 % and dehydrated to a pulp consistency of 20 %.

[0051] As a result thereof, obtained was pulp having a brightness of 86.3 %, a Kappa value of 0.7, a HexA amount of 2.9 $\mu\text{mol/g}$ and a PC value of 1.3.

[Comparative Example 11]

[0052] The same procedure as in Example 10 was carried out, except that the enzyme was not added. As a result thereof, obtained was pulp having a brightness of 84.7 %, a Kappa value of 2.3, a HexA amount of 11.4 $\mu\text{mol/g}$ and a PC value of 3.3.

[0053] As was the case with Example 10 and Comparative Example 11, the finished pulps having no problems in a brightness reversion property were obtained as well in TCF bleaching by introducing the enzyme.

INDUSTRIAL APPLICABILITY

[0054] According to the present invention, unsaturated uronic acid which causes a deterioration in a brightness reversion property of bleached pulp can be removed in producing chemical pulp for papennaking while controlling an increase in a bleaching cost to a minimum level. The present invention is particularly useful in non-chlorine bleaching using mainly chlorine dioxide capable of reducing by-production of organic chlorine compounds which are environmental pollutant.

Claims

1. A method for removing unsaturated uronic acid contained in chemical pulp for papermaking, **characterized by** adding glucuronidase.
2. The method as described in claim 1, wherein glucuronidase contains xylosidase or xylanase.
3. The method as described in claim 1 or 2, wherein glucuronidase contains α -glucuronidase.
4. The method as described in any of claims 1 to 3, wherein unsaturated uronic acid is hexeneuronic acid.
5. The method as described in any of claims 1 to 4, wherein glucuronidase is produced from basidiomycete or filamentous fungus.
6. The method as described in any of claims 2 to 4, wherein xylosidase or xylanase is produced from basidiomycete or filamentous fungus.
7. The method as described in claim 5 or 6, wherein the basidiomycete is a *Cholorosplenium* genus.
8. The method as described in claim 5 or 6, wherein the filamentous fungus is an *Aspergillus* genus.
9. The method as described in claim 7, wherein the *Cholorosplenium* genus is *Cholorosplenium aeruginosum*.
10. The method as described in claim 8, wherein the *Aspergillus* genus is *Aspergillus niger*.
11. The method as described in any of claims 5 to 10, wherein glucuronidase, xylosidase or xylanase is produced on a culture medium containing xylan.
12. The method as described in any of claims 5 to 11, wherein glucuronidase produced is added to the pulp without refining.
13. The method as described in any of claims 1 to 12, wherein glucuronidase is added to the pulp after oxygen treatment, during a bleaching treatment step or after bleaching treatment.
14. The method as described in claim 13, wherein the pulp is ECF bleached pulp or TCF bleached pulp.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 93/11296 A (VALTION TEKNIILLINEN TUTKIMUSKESKUS) 10 June 1993 (1993-06-10) * claims 1-26; examples 1-12 * -----	1-4, 14	INV. D21C5/00 D21H17/22
X	US 2004/069426 A1 (SIIKA-AHO MATTI ET AL) 15 April 2004 (2004-04-15) * claims 1-14; examples 1-8 * -----	1, 2, 4, 14	ADD. D21C9/147
X	WO 91/18978 A (VALTION TEKNIILLINEN TUTKIMUSKESKUS) 12 December 1991 (1991-12-12) * claims 1-9; example 3 * -----	1	
A	US 2003/148453 A1 (MANTYLA ARJA ET AL) 7 August 2003 (2003-08-07) * the whole document * -----	1-14	
A	WO 92/03541 A (VALTION TEKNIILLINEN TUTKIMUSKESKUS) 5 March 1992 (1992-03-05) * the whole document * -----	1-14	
A	US 5 837 515 A (SUOMINEN ET AL) 17 November 1998 (1998-11-17) * the whole document * -----	1-14	TECHNICAL FIELDS SEARCHED (IPC) D21C D21H
A	WO 94/14965 A (GIST-BROCADES N.V; VAN OUYEN, ALBERT, JOHANNES, JOSEPH; DE GRAAFF, LEE) 7 July 1994 (1994-07-07) * the whole document * -----	1-14	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 16 May 2006	Examiner Karlsson, L
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 5
 EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 00 2054

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-05-2006

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9311296	A	10-06-1993	AU 3088292 A	28-06-1993
			CA 2125166 A1	10-06-1993
			EP 0615564 A1	21-09-1994
			FI 89613 B	15-07-1993
			JP 7501587 T	16-02-1995
			NO 942071 A	26-07-1994

US 2004069426	A1	15-04-2004	AT 210216 T	15-12-2001
			AU 2617295 A	04-01-1996
			CA 2191859 A1	14-12-1995
			DE 69524408 D1	17-01-2002
			EP 0764226 A1	26-03-1997
			ES 2169134 T3	01-07-2002
			FI 95607 B	15-11-1995
			WO 9533883 A1	14-12-1995
			PT 764226 T	31-05-2002

WO 9118978	A	12-12-1991	AU 7990391 A	31-12-1991

US 2003148453	A1	07-08-2003	NONE	

WO 9203541	A	05-03-1992	AT 140957 T	15-08-1996
			AU 8421791 A	17-03-1992
			CA 2090493 A1	28-02-1992
			DE 69121205 D1	05-09-1996
			DE 69121205 T2	20-02-1997
			DK 545958 T3	09-12-1996
			EP 0545958 A1	16-06-1993
			ES 2091332 T3	01-11-1996
			FI 904214 A	28-02-1992
			GR 3021510 T3	31-01-1997
			JP 6501609 T	24-02-1994

US 5837515	A	17-11-1998	NONE	

WO 9414965	A	07-07-1994	AU 671710 B2	05-09-1996
			AU 5815494 A	19-07-1994
			CA 2129992 A1	07-07-1994
			FI 943837 A	21-10-1994
			JP 7503860 T	27-04-1995
			NZ 259372 A	25-09-1996
			TW 387939 B	21-04-2000
			US 5610046 A	11-03-1997

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82