(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 863 251 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.09.1998 Bulletin 1998/37

(51) Int Cl.^{6}: **D21C 9/10**

(21) Application number: **98660014.6**

(22) Date of filing: **03.03.1998**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **04.03.1997 JP 48868/97**
25.04.1997 JP 109049/97

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(54) Process for producing bleached pulp

(57) A bleached pulp is produced by a process in which an unbleached pulp prepared from a wood material is treated in an aqueous acid solution under a pressure generated by an oxygen and/or nitrogen containing gas, and the acid-treated pulp is subjected to a single or multi-stage bleaching procedure.

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for producing a bleached pulp. More particularly, the present invention relates to a process for producing a bleached pulp having a high brightness with a high pulp yield by using a decreased amount of a bleaching chemical, while preventing a decrease in viscosity, namely a degree of polymerization, of the pulp.

2. Description of the Related Art

To utilize wood as a material for paper sheets for various uses, the wood is converted to a chemical pulp by using a chemical cooking chemical or to a mechanical pulp by using a mechanical pulping machine, for example, a refiner, and the resultant pulp is bleached with a bleaching chemical to increase the brightness of the pulp.

For example, a kraft pulp produced by cooking wood chips in a kraft cooking liquor is usually, except for the case wherein the kraft pulp is used for the specific paper sheets such as packing paper sheets which are required a high mechanical strength, optionally delignified with oxygen in an aqueous alkali solution, and is necessarily bleached with a bleaching chemical, for example, chlorine, hydrochlorites, chlorine dioxide, oxygen, ozone, and hydrogenperoxide, and a bleaching assistant, for example, sodium hydroxide, in a single stage or in multiple stages, to eliminate lignin which is a pulp-coloring substance from the pulp. The resultant semi-bleached or fully bleached kraft pulps having a Hunter brightness of 70 to 90% are practically useful.

Except for the case where the semi-bleached pulp usable for packing paper sheets, envelopes and paper bags for office use, is produced by bleaching an unbleached pulp with a hydrochlorite in a single stage, usually, the semi-bleached pulp is produced by bleaching an unbleached pulp, which may be a pulp cooked and non-delignified pulp, or a pulp cooked and then delignified with oxygen in an aqueous alkali solution, with a bleaching chemical in two or three stages to such an extent that the Hunter brightness of the bleached pulp reaches about 70 to 80%.

The resultant semi-bleached pulp is used as a bonding pulp for the production of newspaper sheets.

When a fully bleached pulp having a Hunter brightness of about 80 to 90% is produced from an unbleached pulp, it is necessary that a reduction in mechanical strength of the pulp fibers due to the bleaching treatment is minimized. For this reason, the chemical decomposition of hydrocarbon segments, for example, cellulose and hemi-cellulose, from which the pulp fibers are formed should be minimized. Accordingly, severe single stage bleaching should be avoided. Namely, it is preferable that the cooked pulp be delignified with oxygen in an aqueous alkali solution, then, the alkali-oxygen delignified pulp be moderately bleached in 3 to 6 stages by using a bleaching chemical and bleaching conditions chosen so as to minimize the reduction of the mechanical strength of the pulp fibers due to the bleaching.

In a conventional multi-stage bleaching process, usually, an unbleached pulp is first treated with chlorine to chlorinate lignin contained in the pulp fibers, and to impart a solubility in water thereto, then treated with an aqueous alkali solution to dissolve and extract the chlorinated lignin in the aqueous alkali solution, and to remove lignin from the pulp fibers, and finally treated with a hydrochlorite or chlorine dioxide to decompose and remove the residual lignin in the pulp fibers and to obtain a bleached pulp having a high brightness.

However, recently, a problem occurs that organic chlorinated compounds contained in a waste water discharged from the chlorination bleaching procedure of the pulp, may cause environmental pollution and, thus, various new pulp-bleaching processes free from chlorine have been studied. Also, when hydrochlorite is used for bleaching the pulp, chloroform is generated during the pulp-bleaching procedure and may affect the environment. Therefore, a new pulp-bleaching process using no chlorine and no hydrochlorite has been researched.

Currently, the employment of oxygen-containing bleaching chemical, for example, ozone, oxygen, and peroxides, for example, hydrogen peroxide, peracetic acid and persulfuric acid, in place of chlorine and hydrochlorites, is of interest. However, these oxygen-containing bleaching agents except for oxygen and hydrogen peroxide are disadvantageous in a high price and a difficulty in handling due to a danger of explosion and thus have not yet widely utilized in industry. However, -they promise, as bleaching agents for pulp, a bright future. Presently, since the oxygen-containing bleaching agents exhibit a lower selectivity to delignification than chlorine and hydrochlorites, a problem occurs that when the bleaching reaction is excessively effected, the mechanical strength of the pulp fibers decreases to an excessive extent. Therefore, the conditions and sequences of bleaching procedures are still being researched.

Also, there are attempts of reducing the consumption of the bleaching agents while maintaining the brightness of the bleached pulp at a satisfactory level. For example, (1) a method as disclosed in J. E. Jiang et al., Appita, 45 (1), 19 (1992), in which a cooking procedure is carried out under such a condition that the delignification reaction is accelerated, to reduce a Kappa number of the bleached pulp; (2) a method in which the unbleached pulp is delignified with oxygen in an aqueous alkali solution to reduce the Kappa number of the pulp; (3) a method as disclosed, for example, in Japanese Unexamined Patent Publication No. 4-316,690, in which the delignification with oxygen in the aqueous alkali solution is promoted by using a pre-treating chemical such as nitrous acid, to further reduce the Kappa number of the pulp; (4) a method as disclosed, for example, in Japanese Unexamined Patent Publication 2-264,087, in which, before a bleaching step, a pulp is treated with a xylanase; and (5) a method as disclosed, for example, in Japanese Unexamined Patent Publication No. 4-316,689, in which, before a bleaching step, a pulp is treated with a lignin-decomposing enzyme, are disclosed.

The above-mentioned methods, however, should be further improved. For example, the methods in which the delignification in the cooking step is accelerated to a level higher than the conventional level, to obtain a pulp having a reduced Kappa number, are mostly dangerous in that the pulp yield decreases and the resultant pulp fibers exhibit a decreased mechanical strength. Also, the methods in which the delignification is promoted in the oxygen-delignification step in an aqueous alkali solution to decrease the Kappa number of the pulp, are mostly dangerous in that the mechanical strength of the resultant pulp is low. Further, the methods in which before the bleaching step, the pulp is pre-treated with an enzyme, are advantageous in that the pretreatment is carried out under moderate reaction conditions and thus the decreases in the mechanical strength and the yield of the pulp fibers are small. However, the methods are disadvantageous in that the reaction rate is too slow, the reaction time necessary to complete the reaction is too long and the decrease in the Kappa number is very small.

In the treatment of the pulp with the xylanase, which is very interesting, the enzyme must be fully brought into contact with a substrate to initiate the reaction. However, since the xylan and lignin have high molecular weight and are unevenly and three-dimensionally distributed in the pulp fibers and since the enzyme per se is a high molecular compound, it is difficult to bring the xylan or lignin-decomposing enzyme into complete contact with the xylan or lignin in the pulp fibers. Therefore, an improvement of the reaction efficiency of the enzyme is an important subject matter of further research in the future.

Japanese Unexamined Patent Publication No. 6-101,186 discloses a bleaching process for a chemical pulp, in which a unbleached pulp prepared by cooking wood chips is treated at a pulp consistency of 1 to 30% by weight in aqueous acid solution having a pH value of 1 to 5 at a temperature of 30 to 95°C for 5 to 120 minutes, and the acid-treated pulp is delignify-bleached with a peroxide compound and pressurized oxygen in an alkali medium. According to this process, a pulp having a high viscosity and a high brightness can be obtained without bleaching the acid-treated pulp with a bleaching chemical consisting of chlorine or a hydrochlorite. Therefore, in this process, the waste water contains no chlorine-containing organic compound and thus no environmental pollution occurs. However, this process is disadvantageous in that the acid treatment of the unbleached pulp causes substantially no delignification of the unbleached pulp, and thus no decrease in Kapppa number is found in the acid-treated pulp. Therefore, the Kappa number of the acid-treated pulp is similar to that of the unbleached, non-acid-treated pulp.

Also, Japanese Unexamined Patent Publication No. 6-158,573 discloses a process, for delignify-bleaching a pulp, wherein an unbleached pulp prepared by cooking wood chips is delignified with oxygen and an alkali, the alkali oxygen delignified pulp is subjected to an acid treatment under the same conditions as mentioned above, or to a treatment with a cheleting agent, to remove heavy metal ions from the pulp, and then the heavy metal ion-removed pulp is subjected to a delignifying treatment with a peroxide compound or with a peroxide compound and oxygen in an alkali medium.

The acid treatment in the above-mentioned process is carried out for the purpose of removing heavy metal ions from the pulp fibers to prevent a depolymerization of pulp cellulose in the delignify-bleaching procedure with the peroxide compound or with the peroxide compound and oxygen. In this process, the acid treatment per se does not contribute to delignifying the pulp.

A process in which an unbleached pulp prepared by cooking wood chips is delignified with oxygen and an alkali, and then the delignified pulp is treated with an acid in a nitrogen gas atmosphere, to selectively remove hexeneuronic acid which forms xylan side chains of pulp cellulosic compounds, to decrease apparent Kappa number of the pulp and to save the consumption of the bleaching chemical for the bleaching procedure of the pulp, is disclosed, for example, in Tapauni, Vuorinen et al., 1996 International Pulp Bleaching Conference Proceeding, pages 45 to 51.

However, the acid treatment under the conditions as disclosed causes only a decrease in apparent Kappa number of the pulp, but does not contribute to delignifying the pulp. Therefore, the acid treatment does not enhance the bleaching effect on the pulp and the decrease in consumption of the bleaching chemical for the bleaching procedure is unsatisfactory.

Japanese Unexamined Patent Publication No. 6-280,177 discloses a process for bleaching a pulp by acid treating an unbleached pulp prepared by cooking wood chips in an aqueous inorganic acid solution at a pH value of 1.0 to 1.6 at a temperature of 80°C to a boiling temperature of the aqueous acid solution at a pulp consisting of 5 to 20% by weight for 1 to 3 hours, and the acid-treated pulp is subjected to an alkali extraction treatment for lignin in the pulp.

In this process, the acid treatment carried out under the severe conditions of a pH value of 1.0 to 1.6 causes an acid hydrolysis of polysaccharides in the pulp, and thus the yield and the viscosity of the resultant pulp significantly decrease, and the mechanical strength of the pulp may decrease. Further, the acid treatment liquor having a very low pH value needs a large amount of acidic chemicals and thus an economical disadvantage occurs. Also, in this process, the acid treatment which promotes the delignification of the pulp, causes a latent disadvantageous in that the decomposition products of lignin are condensed with each other and are absorbed on the pulp fibers so as to decrease the bleaching effect on the pulp.

Accordingly, there is a great problem that to decrease the consumption of the bleaching chemical for the bleaching procedure by applying a delignification treatment with an acid to the pulp before the bleaching, it is necessary to decrease the degree of acid treatment for the delignificaiton, and to prevent the condensation and absorption of the decomposition products of lignin.

Japanese Unexamined Patent Publication No. 8-158,284 discloses a process for producing a chemical pulp for forming paper, comprising the steps of (1) treating a digested chemical pulp with oxygen in an alkaline condition under high temperature-high pressure conditions; (2) treating the acid treated pulp in a mixture of hydrogen peroxide with a reaction catalyst comprising at least one member selected from oxyacids of IV, V and VI group elements, for example, tungsten, molybdenum, vanadium, selenium and titanium and salts thereof, at a pH value of 3 or less at a temperature of 75 to 110°C; and (3) treating the acid-treated pulp with a peroxide compound in an alkaline medium, in the above-mentioned order.

In this process, when the chemical pulp is delignified with a combination of a peroxide compound with oxygen in an alkaline medium, the chemical pulp is pre-treated with a peroxide compound in the presence of a catalyst under acidic and high temperature conditions. This pre-treatment causes the delignificaiton effect to be significantly enhanced, while generally not decreasing the viscosity of the pulp.

As mentioned above, in the step (2) of this process, the oxyacids of the heavy metals or salts thereof contained in the aqueous acid solution significantly promote the delignification of the pulp. Usually, the acid treatment of the pulp is carried out for the purpose of removing the heavy metals from the pulp, preventing the depolymerization of pulp cellulose due to the presence of heavy metals in the delignify-bleaching step with oxygen, ozone or hydrogen peroxide, and enhancing the quality of the resultant pulp. However, in the above-mentioned process, the heavy metals are intentionally added to the treatment system. Therefore, to prevent the depolymerization of the pulp cellulose in the delignification procedure with the oxidizing agent, a large amount of a protecting agent for the pulp cellulose must be added to the treatment system. Also, when the oxyacids of the heavy metals or the salts thereof are added to the delignification treatment system, a portion of the heavy metals are introduced together with the pulp and/or the waste water from the delignification treatment, into a pulp-producing step or paper-forming step. The introduced heavy metals cause the resultant pulp or paper to be soiled with sticky substances, pitch or scale. Also, since the heavy metals are harmful to the human body, the introduction of the heavy metals into the paper sheets must be severely prevented even when the amount of the introduced heavy metals is small, in a view of health.

Recently, there have been many cases wherein a treatment of the unbleached pulp with oxygen in an aqueous alkali solutions introduced into the pulp-bleaching process. This treatment need an oxygen gas. When the oxygen gas is produced, a nitrogen-containing gas is produced as a by-product. Therefore, it is important to find an industrial utilization of the nitrogen-containing gas.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for producing a bleached pulp, which process is capable of obtaining a bleached pulp having a high brightness with a high yield by using a bleaching chemical in a reduced amount, while preventing or minimizing a reduction in viscosity of the pulp.

The above-mentioned object can be attained by the process of the present invention for producing a bleached pulp, comprising the steps of:

> pulping a wood material to produce an unbleached pulp; and bleaching the unbleached pulp with a bleaching agent in at least one stage,
> wherein before the bleaching step with the bleaching agent, the unbleached pulp is treated with an aqueous acid solution in a gas containing at least one member selected from the group consisting of oxygen and nitrogen under pressure.

In an embodiment of the process of the present invention, before the acid treating step, the unbleached pulp is delignified with oxygen in an aqueous alkali solution and then the acid treatment of the delignified pulp is carried out in an oxygen-containing gas under pressure.

In another embodiment of the process of the present invention, before the acid treating step, the unbleached pulp is delignified with oxygen in an aqueous alkali solution and then the acid treatment of the delignified pulp is carried out in an nitrogen-containing gas under pressure.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventors of the present invention have made an extensive research for improving a delignificaiton of pulp fibers by an acid treatment and a bleaching of the delignified pulp fibers. As a result, it was found that the delignification of the pulp fibers by an acid treatment can be promoted by carrying out the delignification procedure under pressure, to greatly decrease a Kappa number of the pulp, even when no catalyst, for example, a heavy metal, is employed.

In view of the above-mentioned findings, the inventors of the present invention further researched the acid treatment of the wood pulp under pressure in the presence of no catalyst. As a result, it was found that when the acid treatment of the wood pulp is carried out in an oxygen and/or nitrogen-containing gas under pressure, the delignification of the wood pulp is very significantly promoted, and the resultant delignified pulp can be easily bleached with a bleaching chemical by a single or multi-step bleaching procedure, in comparison with the acid-treated pulp under no pressure, and thus the consumption of the bleaching agent could be reduced.

In the bleaching process of the present invention, an unbleached pulp is produced from a wood material by pulping; the unbleached pulp is treated with an aqueous acid solution in a gas containing at least one member selected from the groups consisting of oxygen and nitrogen, under pressure; and

the acid treated pulp is bleached with a bleaching agent in at least one stage.

In the bleaching process of the present invention, optionally, before the acid-treating step, the unbleached pulp is delignified with oxygen in an aqueous alkali solution, and then the delignified pulp is subjected to the acid treating step in an oxygen and/or nitrogen-containing gas under pressure.

The unbleached pulp is produced by subjecting a wood material, for example, wood chips, to a conventional pulping procedure, namely a cooking procedure. The cooking procedure can be carried out by conventional cooking methods, for example, a kraft cooking method, sulfite cooking method, polysulfide cooking method and soda cooking method. In consideration of the quality of the resultant pulp and energy efficiency of the cooking procedure, the kraft cooking method is advantageously utilized.

For example, when a wood material is kraft-cooking, preferably the sulfide degree of the cooking liquor is 5 to 75%, more preferably 15 to 45%, the content of alkali in the cooking liquor is 5 to 30% by weight, more preferably 10 to 25% by weight, based on the bone-dry weight of the wood material, and the cooking temperature is 140 to 170°C. The cooking procedure may be carried out in a continuous cooking method or in a batch-cooking method. When a continuous cooking digester is used, the cooking liquor can be fed into the cooking digester by conventional feeding methods, for example, a modified cooking method in which the cooking liquor is fed through a plurality of feeding inlets.

In the cooking procedure, a cooking additive, for example, a conventional cyclic keto compound, may be added to the cooking liquor.

In the cooking procedure for the wood material, the cooking liquor optionally contains a cooking additive comprising at least one member selected from conventional cyclic keto compounds, for example, benzo-quinone, naphthoquinone, anthraquinone, anthrone, and phenanthroquinone; ring-substituted compounds of the above-mentioned with at least one substitutent, for example, alkyl and amino groups; hydroquinone compounds such as anthrahydroquinone which is one of reduction products of the above-mentioned quinone compounds; and 9,10-diketohydro-anthracene compounds which is a stable compound produced as a by-product of an anthraquinone synthesis by a Diels-Alder method.

The cooking additive is added in an amount of 0.001 to 1.0% by weight based on the bone dry weight of the wood chips to the cooking liquor.

In the process of the present invention, the unbleached pulp delivered from the cooking procedure is washed with water, coarsely screened and then finely screened. The finely screened pulp is optionally subjected, before the acid treatment, to a conventional delignification procedure with oxygen in an aqueous alkali solution. The alkali-oxygen delignification procedure can be carried out in a medium or high consistency. Usually, the alkali-oxygen delignification procedure is preferably carried out in the common medium consistency at a pulp consistency of 8 to 15% by weight.

The alkali usable for the alkali-oxygen delignification in the medium consistency is preferably selected from an aqueous sodium hydroxide solution or an oxidized kraft white liquor. An oxygen gas and an alkali is added into a medium consistency pulp slurry and fully mixed in a medium consistency mixer. Then the pulp-oxygen-alkali mixture is fed into a delignification reactor in which the mixture is held for a certain time, and the delignification reaction is carried out. The medium consistency mixer, of which the constitution is variable in response to manufacturers, has a rotor capable of rotating at a high speed of 500 to 1000 rpm, and can impart a high shearing force to the medium consistency pulp slurry so as to allow the pulp slurry to behave as a fluid such as water, and thus the pulp is fully mixed with the oxygen and the alkali.

In the pulp slurry, preferably the content of oxygen is 0.5 to 3% by weight based on the bone dry weight of the pulp, and the content of the alkali is 0.5 - 4% by dry weight based on the bone dry weight of the pulp. Also, preferably, the reaction temperature is 80 to 120°C, the reaction time is 15 to 100 minutes and the pulp consistency is 8 to 15% by weight. The above-mentioned delignification conditions usable for the present invention include the conventional delignification conditions.

The alkali oxygen-delignified pulp is washed with water and then fed to an acid treatment step in accordance with the present invention.

Also, the unbleached pulp delivered from the cooking procedure, washed with water and screened, may be directly fed to the acid treatment.

In an embodiment (1) of the process of present invention, the acid treatment step is carried out, using no catalyst, by bringing the unbleached pulp (which has optionally been delignified with oxygen in an aqueous alkali solution) into contact with an aqueous acid solution having a pH value of 2 to 6, and treated in an oxygen-containing gas under pressure at a desired temperature for a desired time. The acid treatment of the unbleached pulp with the aqueous acid solution may be carried out by immersing the unbleached pulp in the aqueous acid solution or by impregnating the unbleached pulp with the aqueous acid solution. In the process of the present invention, the acid usable for the acid treatment step is not limited to a specific type of acid, as long as the pH value of the aqueous acid solution can be adjusted to a desired level in the range from 2 to 6. Usually, the acid comprises at least one member selected from inorganic acids, for example, sulfuric acid, nitric acid, hydrochloric acid, sulfurous acid and nitrous acid, and organic acids, for example, acetic acid and formic acid.

Usually, sulfuric acid is advantageously used for the present invention, because the sulfuric is easily available and can be easily handled.

In the acid treatment step of the process of the present invention, the pulp consistency in the treating mixture is preferably 5 to 40% by weight, more preferably 8 to 35% by weight, still more preferably 10 to 25% by weight. When the pulp consistency is less than 5% by weight, the acid treatment must be carried out in a treatment apparatus having a large capacity and thus an economical disadvantage may occur. Also, when the pulp consistency is more than 40% by weight, the large amount of the pulp may be difficult to uniformly mix with the acid solution and thus the effect of the acid treatment may be unsatisfactory.

In the acid treatment of the process of the present invention, to obtain a satisfactory treatment result, the pulp, the oxygen and/or nitrogen contained in the gas and the acid in the aqueous solution must be uniformly mixed in the treatment system. To attain the uniform mixing, a certain mixer selected from, for example, low consistency mixers, medium consistency mixers, static mixers and high consistency mixers is selected in consideration of the types and consistency of the pulp is used. The acid treatment can be carried out under the conditions similar to those of the alkali-oxygen delignification treatment.

In the acid treatment, when the pulp consistency is medium or high, the agitation of the pulp slurry is difficult. In this case, preferably, the pulp slurry, the oxygen and/or nitrogen-containing gas and the aqueous acid solution are mixed by using a medium or high consistency mixer which can impart a high shearing force to the mixture, and then the resultant mixture is fed into a reactor in which a necessary reaction pressure can be held. In this mixing procedure, a disperser may be used or not used. In the reactor, an agitation for further mixing the fed mixture is not carried out, and the fed mixture is held at a desired temperature under a desired pressure for a desired time. In the acid treatment for a medium consistency of pulp, the reactor may be selected from upflow type and downflow type continuous reaction columns which may be equipped with, or free from, a distributer and a discharger.

The reactor usable for the acid treatment of the pulp in a high consistency are preferably selected from vertical down-flow type reactor having a plurality of trays each having an opening and capable of moving downward from an upper tray to a lower tray through the opening by rotating horizontal wings, and Pandia reactor equipped with a plurality of pressure-resistant horizontal tubes and a slowly rotating screw and capable of horizontarily moving the pulp by the slowly rotating screw, of transporting the pulp through the plurality of tubes and of discharging the pulp from the reactor through a final outlet of the tubes.

In an embodiment (1) of the process of the present invention, preferably the acid treatment is carried out at a pulp consistency of 5 to 40% by weight, at a pH value of 2 to 6, more preferably 2.5 to 5, at a temperature of 50 to 150°C, more preferably 90 to 120°C, for a reaction time of 5 to 120 minutes, more preferably 20 to 90 minutes under a pressure on gage generated by an oxygen-containing gas, of 0.5 to 9.0 kg/cm^2, more preferably 1.5 to 7.0 kg/cm^2.

In another embodiment (2) of the process of the present invention, a wood material is pulped into an unbleached pulp; the unbleached pulp is delignified with oxygen in an aqueous alkali solution; the delignified pulp is treated with an aqueous acid solution in a gas containing nitrogen under pressure; and the acid-treated pulp is bleached in at least one stage with a bleaching agent.

In this embodiment (2), preferably the acid treatment is carried out in a pulp consistency of 5 to 40% by weight, at a pH value of 2 to 6, more preferably 2.5 to 5, at a temperature of 50 to 150°C, more preferably 90 to 120°C, for a reaction time of 5 to 120 minutes, more preferably 20 to 90 minutes under a gage pressure of 0.5 to 9.0 kg/cm^2, more preferably 1.5 to 7.0 kg/cm^2, generated by a nitrogen-containing gas.

In the embodiment (2), the nitrogen-containing gas for the acid treatment is not limited to a specific type of nitrogen-containing gas, as long as the nitrogen containing gas has a nitrogen content of 95% by volume or more.

Usually, from an economical point of view, the nitrogen-containing gas is preferably a by-product gas from an oxygen-producing process, for example, a deep cooling isolation method, a PSA (Pressure Swing Absorption) method, or a VSA (Vacuum Swing Absorption) method for producing oxygen.

In the acid treatment in each of the embodiments (1) and (2), when the pH value is less than 2, polysaccharide compounds in the pulp may be decomposed to a higher extent than that of the lignin in the pulp, and thus the mechanical strength and the yield of the resultant pulp fibers may be decreased. Also, when the pH value is more than 6, substantially no delignification of the pulp may occur even under pressure. In this embodiment, since the acid treatment is carried out under pressure generated by an oxygen-containing gas, the delignification of the pulp can be satisfactorily effected even at a high pH value of more than 3, and the resultant acid-treated pulp exhibits an enhanced ease for the bleaching and is thus easily bleached with a conventional bleaching agent to produce a bleached pulp having a high brightness.

When the acid treatment is carried out at a reaction temperature of less than 50°C, the chemical decomposition of lignin with the acid may be insufficient. Also, when the reaction temperature is more than 150°C, the decomposition of the polysaccharide compounds may be significantly promoted, and thus the mechanical strength of the resultant pulp fibers may be unsatisfactory.

In the acid treatment in accordance with the process of the present invention, the reaction time of 5 minutes or more is long enough for completing the acid treatment. However, the extension of the reaction time to more than 120 minutes may not substantially contribute to enhancing the delignification effect, and may cause the resultant pulp fibers to exhibit deteriorated qualities.

In this embodiment, the oxygen-containing gas for imparting a pressure to the acid treatment system may be selected from industrially available oxygen-containing gases having an oxygen content of 20% by volume or more, for example, an oxygen gas prepared by a deep cooling-isolating method, an oxygen gas prepared from PSA (Pressure Swing adsorption), an oxygen gas prepared from VSA (Vacuum Swing adsorption), oxygen or oxygen-containing gases having a degree of purity of oxygen of 85% by volume or more and usable for the conventional alkali-oxygen delignification using oxygen and an alkali, an oxygen-containing gas prepared by a molecular sieve-equipped oxygen-producing apparatus and having an oxygen content of 21% by volume or more, an oxygen-rich gas prepared by mixing air with an oxygen-containing gas having an oxygen content of 85% by volume or more, and air having an oxygen content of 20% by volume or more.

When the bleaching step of the process of the present invention includes an ozone-bleaching stage, the waste gas discharged from the ozone bleaching stage and containing oxygen can be used as an oxygen-containing gas for the acid treatment.

However, in the acid treatment of the process of the present invention, it is important that both the treating pressure of the treatment system and the amount of the oxygen per weight of the pulp in the treatment system be severely adjusted. Therefore, when the oxygen-containing gas has a low oxygen content, and is used in a low partial pressure of oxygen, the treatment pressure must rise to such an extent that the amount of oxygen becomes 0.1% or more per weight of the pulp present in the treatment system.

When the treating pressure of the acid treatment is lower than 0.5 kg/cm^2 on gage, the delignification effect on the pulp by the acid treatment may be insufficient. When the treatment pressure is 9.0 kg/cm^2 on gage or more, the pressurizing effect of the oxygen-containing gas is saturated, the acid treatment apparatus is required to have a high pressure resistance. The pressure resistant apparatus is expensive and thus may cause an economical disadvantage.

The acid-treated pulp is optionally washed with water, and then subjected to a bleaching step with a bleaching agent in a single stage procedure or a multi-stage procedure. Before the bleaching step, the acid-treated pulp is optionally treated with an enzyme, for example, a xylanase and/or a lignin decomposition enzyme.

The bleaching agent usable for the process of the present invention comprises at least one member selected from chlorine (C), hydrochlorite compounds (H), chlorine dioxide (D), oxygen (O), hydrogen peroxide (P), ozone (Z) and organic peroxide compounds. The bleaching agent is optionally used in combination with a bleaching assistant, for example, sodium hydroxide (E).

After the acid treatment under pressure, the resultant acid treated pulp is bleached in a single stage procedure or in a multi-stage procedure. In the multi-stage bleaching procedure, a plurality of bleaching stages different in bleaching agent, bleaching assistant or procedure conditions are carried out in various sequences, for example,

C-E/O-H-D, and C/D-E/O-D wherein chlorine and chlorine-containing bleaching agents are used, or D-E-D, D-E/O-D, E/O-D, E-O-D and Z-D wherein a chlorine-free bleaching agent is used, or Z-E-D, Z-E/O-P or E/OP-PO wherein no chlorine and no chlorine-containing compounds are used.

[Note]

C:	Bleaching stage with atomic chlorine
E/O:	Bleaching stage with oxygen in the presence of sodium hydroxide
H:	Bleaching stage with a hydrochlorite
D:	Bleaching stage with chlorine dioxide

C/D:	Bleaching stage with atomic chlorine and chlorine dioxide
E:	Extraction with sodium hydroxide
O:	Bleaching stage with oxygen
Z:	Bleaching stage with ozone
P:	Bleaching stage with hydrogen peroxide
E/OP:	Bleaching stage with oxygen and hydrogen peroxide in the presence of sodium hydroxide, in an initial portion of which stage, a pressure is applied.
PO:	Bleaching stage with oxygen and hydrogen peroxide in the presence of sodium hydroxide, throughout which stage, a pressure is applied.

In the process of the present invention, the brightness of the pulp bleached by the bleaching step with the bleaching agent can be enhanced by adding an oxidative chemical selected from oxygen and hydrogen peroxide to an alkali-extraction solution, and inserting at least one alkali-extraction stage in a sequence of E/O, E/P or E/OP into the multi-stage bleaching procedure.

The alkali extraction stage using oxygen and/or hydrogen peroxide can be carried out in the method similar to the conventional oxygen-bleaching method under pressure, or in a manner that the pressure is applied only in an initial time of 5 to 15 minutes and then the pressure is reduced to the ambient atmospheric pressure.

In the process of the present invention, waste water discharged from the acid treating step may be recovered. The waste water is optionally fed, together with a waste water recovered from a cooking step, into a boiler for recovered waste, to burn organic substances dissolved or suspended in the waste water and to generate heat energy.

As mentioned above, in the process of the present invention, the acid-treated pulp can be fully bleached by a single or multi-stage bleaching step free from atomic chlorine or from both chlorine and a chlorine-containing bleaching compound. Therefore, when a waste water from the bleaching step is recovered without discharging it to the outside of the bleaching system, the bleaching step can be carried out in a closed system. Also, substantially no pollution due to organic halogen compounds (AOX), derived from the bleaching waste water, occurs.

In the acid-treatment step of the process of the present invention, the unbleached pulp or alkali-oxygen delignified pulp is treated with an aqueous acid solution under pressure generated by an oxygen and/or nitrogen-containing gas. This acid treatment greatly promotes the delignification of the pulp fibers, and the decrease in the Kappa number of the pulp fiber to 20 to 80% based on that of the pulp fibers before the acid treatment. The great decrease in the Kappa number by the acid treatment causes slight decreases in pulp yield and pulp viscosity. However, the decreased Kappa number contributes to significantly decreasing the amount of the bleaching chemicals necessary to the single or multi-stage bleaching procedure. Also, the acid treatment in accordance with the process of the present invention contributes to enhancing the bleachability of the pulp per Kappa number of the pulp, and to increasing the pulp yield in the bleaching procedure. Therefore, in the total yield of the pulp in the acid treatment step and the single or multi-stage bleaching step is similar to the pulp yield in the bleaching step when the acid treatment is omitted.

Particularly, when the pressure for the acid treatment is imparted by a nitrogen-containing gas, the decrease in pulp viscosity by the acid treatment can be minimized, while greatly promoting the delignification of the pulp fibers, and which significantly decreasing the Kappa number of the pulp fibers. Therefore, the decreased Kappa number causes the consumption of the bleaching chemicals in the bleaching step to decrease, while maintaining the pulp strength and yield at a satisfactory level.

In the process of the present invention, the degree of decrease in the Kappa number of the pulp fibers due to the acid treatment in comparison with that before the acid treatment is high for hardwood pulp, and low for other type of pulp. However, even in the other type of pulp, the delignification can be effected. When the oxygen-containing gas is employed, the Kappa number decreasing effects of the acid treatment on various types of pulps are as follows.

Type of pulp	Kappa number before acid treatment	Decrease in % in Kappa number of acid-treated pulp based on that of non-acid treated pulp
Unbleached softwood pulp	20 to 30	20 to 30
Alkali-oxygen delignified, unbleached softwood pulp	12 to 15	20 to 40
Unbleached hardwood pulp	15 to 20	20 to 60
Alkali-oxygen delignified, unbleached hardwood pulp	7 to 11	20 to 80

Also, when the nitrogen-containing gas is used in the acid treatment, the decrease in % in Kappa number of the acid-treated pulp based on that of the non-acid treated pulp is 20 to 70% in the alkali-oxygen delignified, unbleached hardwood pulp and 10 to 30% in the alkali-oxygen delignified, unbleached softwood pulp.

The acid treatment in accordance with the process of the present invention exhibits a significantly high effect on the hardwood pulp, particularly the hardwood pulp delignified with oxygen in an aqueous alkali solution.

In the process of the present invention, the acid treatment under pressure generated by an oxygen and/or nitrogen-containing gas promotes the delignification of the pulp and enhances the bleachability on the acid-treated pulp. The reasons for the above-mentioned effects have not yet been made completely clear but will be made clear by further research in the future. However, it is assumed that first, the delignification reaction with acid is accelerated by applying pressure to the acid treatment system; second, the acid solution can easily penetrate into the inside of the pulp fibers under pressure so as to decompose lignin located not only in the surface portions but also in the inside of the pulp fibers, and third, when the oxygen-containing gas is used, the oxygen is activated by radicals generated by the decomposition of lignin, the activated oxygen accelerates the decomposition of lignin and hinders the condensation reaction of lignin, so that a residual lignin in the pulp fibers after the acid treatment has a easy decomposable structure, or when the nitrogen-containing gas is employed, the inert nitrogen gas fills the acid treatment system and the decomposition of cellulose in the pulp fibers by radicals generated by the decomposition of lignin is prevented.

EXAMPLES

The present invention will be further explained by the following examples which are merely representative and do not restrict the scope of the present invention in any way.

In Examples 1 to 9, an acid treatment was carried out in an oxygen containing gas.

In Examples 1 to 4 and Comparative Examples 1 to 3, the bleaching procedure was carried out in bleaching sequence D1-E-D2.

In Example 5 and Comparative Example 4, the bleaching procedure was carried out in a bleaching sequence D1-E/O-D2.

In Example 6 and Comparative Example 5, the bleaching procedure was carried out in a bleaching sequence E/O-PO.

In Example 7 and comparative Example 6, the bleaching procedure was carried out in a single bleaching stage PO, to produce a semi-bleached pulp.

In each of Examples 8 and 9 and Comparative Examples 7 and 8, a softwood pulp was acid-treated.

In Examples 10 to 13, the acid treatment was carried out in a nitrogen-containing gas.

In Examples 10 and Comparative Example 9, the bleaching procedure was carried out in a bleaching sequence D1-E-D2.

In Example 11, the bleaching procedure was carried out in a bleaching sequence D1-E/O-D2.

In Example 12 and comparative Example 10, the bleaching procedure was carried out in a bleaching sequence E/O-PO.

In Example 13 and Comparative Example 11, the bleaching procedure was carried out in a single stage PO.

Unless specifically indicated, in the examples and comparative examples, the decrease (%) in Kappa number of pulp fibers due to the acid treatment, the decrease (%) in consumption of bleaching chemicals in bleaching stages D1, D2 and E, pulp yield (%) in the acid treatment step, and total yield (%) of pulp in the acid treatment step and the bleaching step, are determined by the following measurement methods.

1. Decrease in % in Kappa number by acid treatment

Kappa numbers of a pulp before and after an acid treatment were determined in accordance with Japanese Industrial Standard (JIS) P 8211, and the decrease in % in Kappa number of the pulp due to the acid treatment was calculated in accordance with the equation (1):

$$\text{Decrease in Kappa number (\%)} = (K_0 - K_1)/K_0 \times 100 \qquad (1)$$

wherein K_0 represents a Kappa number of a pulp before the acid treatment and K_1 represents a Kappa number of the pulp after the acid treatment.

2. Decrease (%) in bleaching chemical consumption in beaching stages D1 and D2

A total amount (A_0) of chlorine dioxide consumed in bleaching stages D1 and D2 for a pulp before the acid treatment, and a total amount (A_1) of chlorine dioxide consumed in bleaching stages D1 and D2 for a pulp after the acid treatment were determined. Then, a decrease (%) in consumption of chlorine dioxide in the bleaching stages D1 and D2 due to the acid treatment was calculated in accordance with the equation (2):

$$\text{Decrease in chlorine dioxide consumption (\%)} = (A_0 - A_1)/A_0 \times 100 \qquad (2)$$

3. Decrease in % consumption of bleaching chemicals in bleaching stage E

A amount (a_0) of sodium hydroxide used in a bleaching stage E for a pulp before the acid treatment and an amount (a_1) of sodium hydroxide used in a bleaching stage E for a pulp after the acid treatment were determined.

A decrease (%) in consumption of sodium hydroxide in the bleaching stage E due to the acid treatment was calculated in accordance with the equation (3):

$$\text{Decrease in sodium hydroxide consumption (\%)} = (a_0 - a_1)/a_0 \times 100 \qquad (3)$$

4. Pulp yield (%) in acid treatment

A bone dry weight (W_0) of a pulp fed to the acid treatment and a bone dry weight (W_1) of the pulp delivered from the acid treatment were determined.

A pulp yield (%) in the acid treatment was calculated in accordance with the equation (4):

$$\text{Pulp yield (\%) in acid treatment} = W_1/W_0 \times 100 \qquad (4)$$

5. Total pulp yield (%) in acid treatment and bleaching procedures

A total pulp yield in the acid treatment and bleaching procedures were calculated in accordance with the equation (5):

$$\text{Total pulp yield (\%) in acid treatment and bleaching procedures} = (Y_1 \times Y_2)/100 \qquad (5)$$

In the equation (5), Y_1 represents a yield of the pulp in the acid treatment step and Y_2 represent a yield of the pulp in the bleaching step.

Example 1

Mixed hardwood chips comprising 70% by weight of Japan-produced hardwood chips and 30% by weight of eucalyptus wood chips and in a bone dry weight of 500g was kraft-cooked in a laboratory indirect-heating autoclave containing a cooking liquor having an effective alkali content of 18% based on the bone dry weight of the wood chips, a degree of sulfidity of 25% and a liquor ratio of 4 to the bone dry weight of the wood chips at a cooking temperature of 160°C for a cooking time of 120 minutes. The resultant pulp was collected, and finely screened through a flat screen equipped with a 10 cuts screen plate. An unbleached hardwood kraft pulp having a Hunter brightness of 45.2%, a Kappa number of 20.1, a pulp viscosity of 23.3 mPa·s (determined in accordance with J. TAPPI, 44) was obtained in an amount of 229g in a finely screened pulp yield of 45.8%.

The unbleached pulp in a bone dry weight of 80.0g was suspended in a pulp consistency of 10% by weight in an acid treatment solution prepared by dissolving concentrated sulfuric acid in ion-exchanged water, having a pH value of 2.6 and contained in a stainless steel indirect heating autoclave having a capacity of 2 liters. Into the autoclave, a compressed oxygen gas having a degree of purity of oxygen of 99.9% was introduced under a pressure of 5kg/cm^2 on gage, and the pulp was acid-treated with the aqueous sulfuric acid solution at a temperature of 105°C under the above-mentioned pressure on gage for 60 minutes. After the autoclave was cooled, the acid-treated pulp was washed with ion-exchanged water and dewatered.

An acid-treated pulp having a Hunter brightness of 48.1%, a Kappa number 11.0 and a pulp viscosity of 17.8 mPa·s was obtained in a bone dry weight of 78.9g. The decrease in Kappa number due to the acid treatment was 45.3% and the pulp yield in the acid treatment was 98.6%.

The acid treated pulp in a bone dry weight of 70.0g was placed in a plastic resin bag and suspended in a pulp consistency of 10% by weight in ion-exchanged water, then chlorine dioxide is added in an amount of 1.10% based on the bone dry weight of the pulp to the pulp slurry in the bag. The pulp slurry-containing bag was immersed in a constant temperature water bath at a temperature of 70°C for 30 minutes, to carry out a bleaching stage D1 procedure. The D1-bleached pulp was washed with ion-exchanged water and dewatered. The resultant DI-bleached pulp was in a bone dry weight of 69.5g.

The D1-bleached pulp in a bone dry weight of 69.5g was placed in a plastic resin bag and suspended in a pulp consistency of 10% by weight in ion-exchanged water. Then, sodium hydroxide was added in an amount of 1.7 times the amount of chlorine dioxide used in the D1 stage to the pulp slurry. The resultant pulp slurry was treated with the sodium hydroxide at a temperature of 70°C for 120 minutes in the same manner as in the D1 stage, to carry out an extraction procedure in an E stage. The resultant pulp after the E stage was washed with ion-exchanged water and dewatered. A E stage-extracted pulp was obtained in a bone dry weight of 68.8g.

The E stage-extracted pulp in a bone dry weight of 68.8g was placed in a plastic resin bag and suspended in a pulp consistency of 10% by weight in ion-exchanged water. Then, chlorine dioxide was added in an amount of 0.7% based on the bone dry weight of the pulp to the pulp slurry. The resultant pulp slurry was treated with chlorine dioxide at a temperature of 70°C for 180 minutes to effect a D2 stage bleaching procedure. The resultant pulp was washed with ion-exchanged water and dewatered to obtain a bleached pulp in a bone dry weight of 68.5g.

The pulp yield of the multi-stage bleaching procedure was 97.9% and the total pulp yield of the acid treatment and bleaching procedures was 96.5%.

The D2 stage bleached pulp was disintegrated and then formed into a pulp sheet having a basis weight of 60 g/m^2 in accordance with TAPPI Testing Method T 205 os - 71 (JIS P 8209). The pulp sheet had a brightness of 85.4% determined in accordance with JIS P8123.

In Table 1, the Kappa number of the acid treated pulp, the decrease in Kappa number due to the acid treatment and pulp yield in the acid treatment are shown. Also, in Table 2, the amounts of the bleaching chemicals used in the D1 and D2 stages in the bleaching procedure, the decrease in the total bleaching chemical consumption in the D1 and D2 stages in the bleaching procedure, the decrease in bleaching chemical consumption in the E-stage in the bleaching procedure, the pulp yield of the bleaching procedure and the total pulp yield of the acid treatment and bleaching procedures are shown.

Example 2

The same unbleached hardwood kraft pulp as in Example 1 was suspended in a bone dry weight of 90.0g in ion-exchanged water, and added with sodium hydroxide in an amount of 1.5% based on the bone dry weight of the pulp. The aqueous unbleached pulp slurry was diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight.

The pulp slurry was placed in an indirect heating autoclave and pressurized by introducing a compressed oxygen gas having a degree of purity of oxygen of 99.9% to a pressure on gage of 5 kg/cm^2 and heated at a temperature of 100°C for 60 minutes, to delignify the unbleached pulp by a medium consistency alkali-oxygen-delignifying method.

The resultant lignified pulp was washed with ion-exchanged water, and dewatered. An oxygen lignified pulp having a Hunter brightness of 51.1%, a Kappa number of 10.2, and a pulp viscosity of 18.8 mPa·s was obtained in a bone dry weight of 88.8g.

The alkali-oxygen lignified pulp in a bone dry weight of 80.0g was suspended in ion-exchanged water, and the pulp slurry was diluted with an aqueous acid solution prepared by dissolving concentrated sulfuric acid in ion-exchanged water to adjust the pH value of the slurry to 2.6 and the pulp consistency of the slurry to 10% by weight. The pulp slurry was placed in an indirect heating stainless steel autoclave having a capacity of 2 liters, and a commercially available compressed oxygen gas having a degree of purity of oxygen of 99.9% was introduced into the autoclave to adjust the pressure on gage of the autoclave to 5 kg/cm^2, and then the pulp slurry was heated at a temperature of 95°C for 60 minutes while maintaining the pressure on gage at the above-mentioned level, to apply an acid treatment under pressure to the delignified pulp. After the autoclave was cooled, the resultant acid-treated pulp was washed with ion-exchanged water and dewatered.

An acid-treated pulp having a Hunter brightness of 53.4%, a Kappa number of 4.3 and a pulp viscosity of 15.8 mPa·s was obtained in a bone dry weight of 79.2g at a decrease in Kappa number of 57.8% with a pulp yield of 99.0%.

The acid-treated pulp in a bone dry weight of 70.0g was subjected to the same D1 stage bleaching procedure in Example 1 except that the amount of chlorine dioxide used was 0.3% based on the bone dry weight of the pulp, and washed with ion-exchanged water and dewatered, to obtain a D1 stage bleached pulp in a bone dry weight of 69.9g.

The D1 stage bleached pulp in a bone dry weight of 69.9g was subjected to the same E stage extraction procedure as in Example 1, and washed with ion-exchanged water and dewatered to obtain an E stage extracted pulp in a bone dry weight of 69.7g.

The E stage extracted pulp in a bone dry weight of 69.7g was subjected to the same D2 stage bleaching procedure except that chlorine dioxide was employed in an amount of 0.40% based on the bone dry weight of the pulp.

After washing and dewatering, a bleached pulp was obtained in a bone dry weight of 69.6g. The pulp yield in the multi-stage bleaching procedure was 99.4% and the total pulp yield in the acid treatment and bleaching procedures was 98.4%.

The D2-stage bleached pulp was disintegrated and formed into a pulp sheet having a basis weight of 60 g/m^2 in the same manner as in Example 1 and a brightness of the pulp sheet was determined in accordance with the TAPPI testing method. The brightness was 85.5%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment, and the pulp yield in the acid treatment. Also, Table 2 shows the amounts of the bleaching chemicals used in the D1 and D2 bleaching stages, the decrease in bleaching chemical consumption in the bleaching procedure, the decrease in bleaching chemical consumption in the E stage, the pulp yield in the bleaching step and the total pulp yield in the acid treatment and bleaching procedures.

Example 3

The delignified pulp prepared by the same alkali-oxygen delignification procedure as in Example 2, and having a Kappa number of 10.2 was subjected to the same acid-treatment and multi-stage (D1-E-D2) bleaching procedures as in Example 2, except that the acid treating temperature was changed to 105°C and the amount of chlorine dioxide employed in the D1 stage bleaching was changed to 0.18% based on the bone dry weight of the pulp, to obtain a bleached pulp.

The Kappa number of the acid-treated pulp was 2.6, the decrease in Kappa number due to the acid treatment was 74.5%, the acid-treated pulp was obtained in a bone dry weight of 79.0g at a pulp yield of 98.8%. The multi-stage bleached pulp was obtained in a bone dry weight of 69.7g and in a pulp yield of 99.6% and had a Hunter brightness of 85.6%. The total yield of the pulp in the acid treatment and bleaching procedures was 98.4%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Also, Table 2 shows the amounts of the bleaching chemical used in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the E stage, the pulp yield in the acid treatment and the total pulp yield in the acid treatment and bleaching procedures.

Example 4

The same alkali-oxygen delignified pulp as in Example 2 having a Kappa number of 10.2 was subjected to the same acid treatment as in Example 2, except that air was used in place of the oxygen gas, and in the D1 stage, the amount of chlorine dioxide used was 0.33% based on the bone dry weight of the pulp. The acid-treated pulp was subjected to the same multi-stage (D1-E-D2) bleaching procedure as in Example 2, to produce a bleached pulp.

The Kappa number of the acid-treated pulp was 4.4, the decrease in Kappa number due to the acid treatment was 56.9%, the acid-treated pulp was obtained in a bone dry weight of 79.2g at a pulp yield of 99.0%. The multi-stage bleached pulp was obtained in a bone dry weight of 69.5g and in a pulp yield of 99.3% and had a Hunter brightness of 85.5%. The total yield of the pulp in the acid treatment and bleaching procedures was 98.3%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Also, Table 2 shows the amounts of the bleaching chemical used in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the E stage, the pulp yield in the acid treatment and the total pulp yield in the acid treatment and bleaching procedures.

Example 5

The same acid-treated pulp having a Kappa number of 4.3 and prepared at a decrease in Kappa number of 57.8% in a pulp yield of 99.0%, as in Example 2 was subjected in a bone dry weight of 70g to the same multi-stage (D1-E-D2) bleaching procedure as in Example 2 with the following exceptions.

The D1 stage-bleached-pulp was subjected to an alkali extraction procedure (E/O) in the presence of oxygen. In the alkali extraction procedure, sodium hydroxide was added in an amount of 0.51% based on the bone dry weight of the pulp to the D1 stage-bleached pulp slurry, the pulp slurry was diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10%, the pulp slurry was placed in an indirect heating autoclave, pressurized with a compressed oxygen gas having a degree of purity of oxygen of 99.9% to a pressure on gage of 1.5 kg/cm^2, and heated at a temperature of 70°C for 15 minutes under the above-mentioned pressure. Then, the pressure of the autoclave was released, and the pulp slurry was further heated at a temperature of 70°C for 105 minutes under ambient atmospheric pressure (pressure on gage = zero).

After the alkali extraction (E/O) in the presence of oxygen was completed, the resultant pulp was subjected to the same D2 stage bleaching procedure as in Example 2, except that the amount of chlorine dioxide used was changed to 0.10% by weight.

The bleached pulp having a brightness of 85.4% was obtained in a bone dry weight of 69.5g in a pulp yield of 99.3%. The pulp yield in the multi-stage bleaching procedure was 99.3% and the total pulp yield in the acid treatment and bleaching procedures was 98.3%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Also, Table 2 shows the amounts of the bleaching chemical used in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the E stage, the pulp yield in the acid treatment and the total pulp yield in the acid treatment and bleaching procedures.

Example 6

The same acid-treated pulp having a Kappa number of 4.3 and prepared at a decrease in Kappa number of 57.8% and in a pulp yield of 99.0%, as in Example 2, was subjected in a bone dry weight of 70g to an alkali extraction (E/OP) in the presence of oxygen and hydrogen peroxide. In the alkali extraction (E/op), the acid-treated pulp slurry was added with 1.0% of sodium hydroxide and 0.5% of hydrogen peroxide, based on the bone dry weight of the pulp, and diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight, the resultant pulp slurry was placed in an indirect heating autoclave, pressurized with a compressed oxygen gas having a degree of purity of oxygen of 99.9% to a pressure on gage of 1.5 kg/cm^2, and heated at a temperature of 70°C under the above-mentioned pressure for 15 minutes. After the pressure was released, the pulp slurry was held at a temperature of 70°C under ambient atmospheric pressure for 105 minutes. After the alkali extraction (E/OP) was completed, the autoclave was cooled, the resultant alkali-extracted pulp was washed with ion-exchanged water, and dewatered to obtain the (E/op) alkali extracted pulp in a bone dry weight of 69.4g.

The (E/PO) alkali-extracted pulp in a bone dry weight of 69.4g was subjected to a hydrogen peroxide bleaching stage (PO) under pressure generated by an oxygen gas.

In the bleaching stage (PO), an aqueous slurry of the (E/OP) alkali-extracted pulp was added with 1.5% of sodium hydroxide and 3.0% of hydrogen peroxide based on the bone dry weight of the pulp, diluted with ion-exchanged water to adjust the pulp consistency to the slurry to 10% by weight. The resultant pulp slurry was placed in an indirect heating autoclave, pressurized with a compressed oxygen gas having a degree of purity of oxygen of 99.7% to a pressure on gage of 5 kg/cm^2, and then heated at a temperature of 100°C under the above-mentioned pressure for 60 minutes.

The resultant PO stage bleached pulp was washed with ion-exchanged water, and dewatered. A bleached pulp having a Hunter brightness of 85.4% was obtained in a bone dry weight of 69.1g. The pulp yield in the bleaching (E/OP-PO) procedure was 98.7% and the total pulp yield in the acid treatment and bleaching procedure was 97.7%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Also, Table 3 shows the total pulp yield in the acid treatment and bleaching procedures and the brightness of the pulp.

Example 7

The same acid-treated pulp having a Kappa number of 4.3 and prepared in a decrease in Kappa number of 57.4% and with a pulp yield of 99.0% as in Example 2 was subjected in a bone dry weight of 70g to a hydrogen peroxide bleaching procedure (a PO-bleaching stage) under a pressure imparted by an oxygen gas.

In the PO bleaching stage, an aqueous slurry of the acid-treated pulp was added with 1.5% of sodium hydroxide and 2.0% of hydrogen peroxide based on the bone dry weight of the pulp, diluted with ion-exchanged water to adjust the pulp consistency of 10% by weight. The resultant pulp slurry was placed in an indirect heating autoclave, pressurized with a compressed oxygen gas having a degree of purity of oxygen of 99.9% to a pressure on gage of 5 kg/cm^2, and heated at a temperature of 100°C under the above-mentioned pressure for 60 minutes.

The (PO)-bleached pulp was washed with ion-exchanged water and dewatered. A semi-bleached pulp having a Hunter brightness of 75.2% was obtained in a bone dry weight of 69.6g.

The pulp yield in the PO bleaching procedure was 99.4% and the total pulp yield in the acid-treatment and bleaching procedures was 98.4%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Also, Table 3 shows the total pulp yield in the acid treatment and bleaching procedures and the rightness of the pulp.

Example 8

Mixed softwood chips comprising 60% by weight of Japan-produced softwood chips and 40% by weight of radiata pine wood chips and in a bone dry weight of 500g was kraft-cooked in a laboratory indirect-heating autoclave containing a cooking liquor having an effective alkali content of 20% based on the bone dry weight of the wood chips, a degree of sulfidity of 25% and a liquor ratio of 5 to the bone dry weight of the wood chips at a cooking temperature of 165°C for a cooking time of 150 minutes. The resultant pulp was collected, and finely screened through a flat screen equipped with a 14 cuts screen plate. An unbleached softwood kraft pulp having a Hunter brightness of 43.3%, a Kappa number of 27.5, a pulp viscosity of 31.6 mPa·s (determined in accordance with J. TAPPI, 44) was obtained in an amount of 218g in a finely screened pulp yield of 43.6%.

The unbleached pulp in a bone dry weight of 80.0g was suspended in a pulp consistency of 10% by weight in an acid treatment solution prepared by dissolving concentrated sulfuric acid in ion-exchanged water, having a pH value of 2.6 and contained in a stainless steel indirect heating autoclave having a capacity of 2 liters. Into the autoclave, a compressed oxygen gas having a degree of purity of oxygen of 99.9% was introduced under a pressure of 5 kg/cm^2 on gage, and the pulp was acid-treated with the aqueous sulfuric acid solution at a temperature of 105°C under the above-mentioned pressure on gage for 60 minutes. After the autoclave was cooled, the acid-treated pulp was washed with ion-exchanged water and dewatered.

An acid-treated pulp having a Hunter brightness of 46.2%, a Kappa number 18.3, and a pulp viscosity of 22.3 mPa·s was obtained in a bone dry weight of 78.6g. The decrease in Kappa number due to the acid treatment was shown in Table 4.

Example 9

The same unbleached softwood kraft pulp as in Example 8 in a bone dry weight of 90g was suspended in ion-exchanged water. The resultant pulp slurry was added with 2.1% of sodium hydroxide based on the bone dry weight of the pulp, diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight, and then placed in an indirect heating autoclave. The pulp slurry in the autoclave was pressurized with a compressed oxygen gas having a degree of purity of oxygen of 99.9% to a pressure on gage of 5 kg/cm^2, and heated at a temperature of 100°C under the above-mentioned pressure for 60 minutes to delignify the pulp fibers in accordance with the medium consistency alkali-oxygen bleaching method. The delignified pulp was washed with ion-exchanged water and dewatered. The alkali-oxygen delignified pulp was obtained in a bone dry weight of 88.5g and had a Hunter brightness of 48.8%, a Kappa number of 13.3 and a pulp viscosity of 21.8 mPa·s.

The alkali-oxygen delignified pulp in a bone dry weight of 80.0g was suspended in ion-exchanged water and diluted with an aqueous sulfuric acid solution prepared by dissolving concentrated sulfuric acid in ion-exchanged water and having a pH value of 2.6, to adjust the pulp consistency in the slurry to 10% by weight.

The resultant pulp slurry was placed in a stainless steel indirect heating autoclave having a capacity of 2 liters, pressurized with a compressed oxygen gas having a degree of purity of oxygen of 99.9% to a pressure on gage of 5 kg/cm^2, and heated at a temperature of 105°C under the above-mentioned pressure for 60 minutes, to acid-treat the pulp.

After the autoclave was cooled, the resultant acid-treated pulp was washed with ion-exchanged water and dewatered.

The resultant acid-treated pulp was collected in a bone dry weight of 79.2g and had a Hunter brightness of 51.3%, a Kappa number of 8.2 and a pulp viscosity of 17.1 mPa·s. In the acid treatment, the decrease in Kappa number of the pulp, and the pulp yield are shown in Table 4.

Comparative Example 1

The same procedures as in Example 1 were carried out to produce a bleached pulp, with the following exceptions.

The acid treatment for the unbleached pulp was omitted.

In the D1 stage bleaching procedure, the bleaching chemical (chlorine dioxide) was employed in an amount of 2.41% based on the bone dry weight of the pulp. The bleaching procedure was carried out in the same sequence D1-E-D2 as in Example 1.

The resultant bleached pulp was collected in a bone dry weight of 67.5g with a pulp yield of 96.4% and had a

Hunter brightness of 85.4%.

Table 1 shows the Kappa number of the unbleached pulp, and Table 2 shows the amounts of the bleaching chemical used in the D1 and D2 stage procedures and pulp yield in the whole bleaching procedures.

Comparative Example 2

The same procedures as in Example 2 were carried out to produce a bleached pulp, with the following exceptions.

The acid treatment for the alkali-oxygen delignified pulp was omitted.

In the D1 stage bleaching procedure, the bleaching chemical (chlorine dioxide) was employed in an amount of 0.92% based on the bone dry weight of the pulp. The bleaching procedure was carried out in the same sequence D1-E-D2 as in Example 2.

The resultant bleached pulp was collected in a bone dry weight of 68.7g with a pulp yield of 98.1% and had a Hunter brightness of 85.3%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Also, Table 2 shows the amounts of the bleaching chemical used in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the E stage, the pulp yield in the acid treatment and the total pulp yield in the acid treatment and bleaching procedures.

Comparative Example 3

A bleached pulp was produced by the same procedure as in Example 2, with the following exceptions.

In the acid treatment, the pressurization with the compressed oxygen gas was omitted, and the amount of the bleaching chemical (chlorine dioxide) used in the D1 stage bleaching procedure was 0.65% based on the bone dry weight of the pulp. The bleaching was carried out in the same sequence D1-E-D2 in Example 2.

The resultant bleached pulp having a Hunter brightness of 85.3% was obtained in a bone dry weight of 69.lg.

The acid-treated pulp had a Kappa number of 6.5. The decrease in Kappa number due to the acid treatment was 36.3%. The bone dry weight of the acid treated pulp was 79.4g. The pulp yield in the acid treatment was 99.3%. The bone dry weight of the bleached pulp was 69.1g. The pulp yield in the multi-stage bleaching procedure was 98.7% and the total pulp yield in the acid treatment and bleaching procedures was 98.0%.

Table 1 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid treatment and pulp yield in the acid treatment. Also, Table 2 shows the amounts of the bleaching chemical (chlorine dioxide) used in the D1 and D2 stage bleaching procedures, the decrease in bleaching chemical consumption in the D1 and D2 stage bleaching procedures, the decrease in bleaching chemical consumption in the E stage procedure, the pulp yield in the bleaching procedure and the total pulp yield in the acid treatment and bleaching procedures.

Comparative Example 4

The same acid treated pulp having a Kappa number of 6.5 and prepared with a decrease in Kappa number of 36.3% and a pulp yield of 99.3%, as in Comparative Example 3 was subjected in a bone dry weight of 70g to the same D1 stage procedure as in Comparative Example 3.

The D1 stage-bleached pulp slurry was added with 1.11% of sodium hydroxide based on the bone dry weight of the pulp and diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight.

The pulp slurry was placed in an indirect heating autoclave, pressurized with a compressed oxygen gas having a degree of purity of oxygen of 99.9% to a pressure on gage of 1.5 kg/cm^2, and heated at a temperature of 70°C under the above-mentioned pressure for 15 minutes. The pressure in the autoclave was reduced and the pulp slurry was heated at a temperature of 70°C under ambient atmospheric pressure (pressure on gage = 0) for 105 minutes, to apply an alkali extraction (E/O) in the presence of oxygen to the pulp. Then, the alkali-extracted pulp was subjected to the same D2 stage bleaching procedure as in Example 2, except that the amount of chlorine dioxide was changed to 0.28% based on the bone dry weight of the pulp.

As a result of the above-mentioned multi-stage bleaching procedure in the sequence D1-E/O-D2, a bleached pulp having a Hunter brightness of 85.4% was collected in a bone dry weight of 69.1g.

The pulp yield in the multi stage bleaching procedure was 98.7%, and the total pulp yield in the acid treatment and bleaching procedures was 98.0%.

In Table 1, the Kappa number of the acid treated pulp, the decrease in Kappa number due to the acid treatment and pulp yield in the acid treatment are shown. Also, in Table 2, the amounts of the bleaching chemicals used in the D1 and D2 stages of the bleaching procedure, the decrease in the total bleaching chemical consumption in the D1 and D2 stages in the bleaching procedure, the decrease in bleaching chemical consumption in the E/O-stage in the bleaching, the pulp yield of the bleaching procedure and the total pulp yield of the acid treatment and bleaching procedures are shown.

Comparative Example 5

The same acid treated pulp having a Kappa number of 6.5 and prepared with a decrease in Kappa number of 36.3% and a pulp yield of 99.3%, as in Comparative Example 3 was subjected in a bone dry weight of 70g to the same multi-stage bleaching procedure in the sequence E/OP-PO as in Example 6.

As a result of the above-mentioned multi-stage bleaching procedure, a bleached pulp having a Hunter brightness of 81.4% was collected in a bone dry weight of 68.9g.

The pulp yield in the multi stage bleaching procedure was 98.4%, and the total pulp yield in the acid treatment and bleaching procedures was 97.7%.

Table 3 shows the Hunter brightness of the multi-stage bleached pulp and the total pulp yield in the acid treatment and bleaching procedures.

Comparative Example 6

The same acid treated pulp having a Kappa number of 6.5 and prepared with a decrease in Kappa number of 36.3% and a pulp yield of 99.3%, as in Comparative Example 3 was subjected in a bone dry weight of 70g to the same single stage (PO) bleaching procedure as in Example 7.

As a result of the above-mentioned single-stage bleaching procedure, a bleached pulp having a Hunter brightness of 69.8% was collected in a bone dry weight of 69.5g.

The pulp yield in the bleaching procedure was 99.3%, and the total pulp yield in the acid treatment bleaching procedures was 98.6%.

Table 3 shows the Hunter brightness of the bleached pulp and the total pulp yield in the acid treatment and bleaching procedures.

Comparative Example 7

The same acid treatment as in Example 8 was carried out, except that the pressurization with the compressed oxygen gas for the acid treating system was omitted.

An acid treated pulp having a Hunter brightness of 43.3%, a Kappa number of 21.8 and a pulp viscosity of 23.8 mPa·s was collected in a bone dry weight of 78.7g.

Table 4 shows the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Comparative Example 8

The same acid treatment as in Example 9 was carried out, except that the pressurization with the compressed oxygen gas to the acid treating system was omitted.

An acid treated pulp having a Hunter brightness of 48.8%, a Kappa number of 10.0 and a pulp viscosity of 18.0 mPa·s was collected in a bone dry weight of 69.4g.

Table 4 shows the decrease in Kappa number due to the acid treatment and the pulp yield in the acid treatment.

Table 1

Item / Example No.		Unbleached, non-acid-treated pulp		Unbleached, acid-treated pulp			
		Kappa number	Pulp viscosity (mPa·s)	Kappa number	Decrease in Kappa number (%)	Pulp viscosity (mPa·s)	Pulp yield (%)
Example	1	20.1	23.3	11.0	45.3	17.8	98.6
	2	10.2	18.8	4.3	57.8	15.8	99.0
	3			2.6	74.5	14.7	98.8
	4			4.4	56.9	16.1	99.0
	5			4.3	57.8	15.8	99.0
	6			4.3	57.8	15.8	99.0
	7			4.3	57.8	15.8	99.0
Comparative Example	1	20.1	23.3	-	-	23.3	-
	2	10.2	18.8	-	-	18.8	-
	3			6.5	36.3	16.8	99.3
	4			6.5	36.3	16.8	99.3
	5			6.5	36.3	16.8	99.3
	6			6.5	36.3	16.8	99.3

Table 2

Item / Example No.		Multi stage (D1-E-D2) Bleaching					Total pulp yield in acid treatment and bleaching procedures (%)
		Amount of chemical used		Decrease in consumption of chemicals		Pulp yield (%)	
		D1-stage	D2-stage	D1 and D2-stage	E-stage		
Example	1	1.10	0.7	42.1	54.4	97.9	96.5
	2	0.30	0.4	47.0	67.4	99.4	98.4
	3	0.18	0.4	56.1	80.4	99.6	98.4
	4	0.33	0.4	44.7	64.1	99.3	98.3
	5	0.30	0.10	69.7	67.4	99.3	98.3
Comparative Example	1	2.41	0.7	-	-	96.4	96.4
	2	0.92	0.4	-	-	98.1	98.1
	3	0.65	0.4	20.5	29.3	98.7	98.0
	4	0.65	0.28	29.5	29.3	98.7	98.0

Table 3

Item / Example No.		Acid-treated, multi-stage bleached pulp	
		Brightness (%)	Total pulp yield (%)
Example	6	85.4	97.7
	7	75.2	98.4
Comparative Example	5	81.4	97.7
	6	69.8	98.6

Table 4

Item / Example No.		Acid-treated pulp	
		Decrease in Kappa number (%)	Pulp yield (%)
Example	8	33.5	98.3
	9	38.3	99.0
Comparative Example	7	20.7	98.4
	8	24.8	99.1

Tables 1 to 4 clearly show that when a hardwood pulp is subjected to the process of the present invention, as Examples 1 to 7 show, by acid treating an unbleached hardwood pulp having a Kappa number of 20.1 or an alkali-oxygen delignified hardwood pulp having a Kappa value of 10.2, under pressure imparted by an oxygen gas, the delignification of the pulp was enhanced, while the pulp viscosity slightly decreased, so as to decrease the Kappa number of the pulp by 45.3 to 74.5%. When a single or multi-stage bleaching procedure with a bleaching chemicals was applied to the acid-treated pulp, the brightness of the pulp could be increased to a desired level, with a significantly reduced amount of bleaching chemicals, while maintaining the pulp viscosity and the pulp yield at satisfactory levels.

Also, as shown in Example 5, the pulp acid-treated in the presence of oxygen under pressure exhibited a significantly enhanced delignification property in the alkali extraction stage (E/O) in the presence of oxygen in the multi-stage bleaching procedure, and thus the amount of the bleaching chemicals necessary to bleach the pulp into a desired brightness could be greatly reduced. Further, as Example 6 clearly shows, when the acid treatment in the presence of oxygen under pressure was applied to the alkali-oxygen delignified pulp in accordance with the process of the present invention, the resultant acid-treated pulp could be bleached to a desired brightness of 85.4% by a multi-stage bleaching procedure in a sequence E/PO-PO, without using chlorine and chlorine-containing chemicals as a bleaching chemical.

Compared with this, as shown in Comparative Example 5, when the pressurization with oxygen gas is omitted in the acid treatment, the same multi stage bleaching procedure (E/op-PO) as in Example 6 resulted in a reduced pulp brightness of 81.4% which was unsatisfactory.

Also, in comparative Examples 3 and 4 wherein the acid treatment of the pulp is carried out without pressurizing with the oxygen gas, the decrease in Kappa number of the pulp due to the acid treatment was 36% which was lower than that in the case where the pressurization with the oxygen gas is carried out. As shown in Comparative Example 4, the decrease in the bleaching chemical consumption in the multi-stage bleaching procedure is very low. As shown Comparative Example 4, even when an alkali-extraction stage (E/O) in the presence of oxygen is inserted into the multi-stage bleaching procedure, the decrease in the bleaching chemical consumption was unsatisfactory.

As shown in Example 7, the acid treatment in accordance with the process of the present invention enables the acid treated pulp to be bleached by a hydrogen peroxide bleaching procedure under pressure generated by oxygen gas to produce a semi-bleached pulp with a brightness of 75%. However, as shown in Comparative Example 6, when the acid treatment was carried out without pressurizing with the oxygen gas, and the acid treated pulp was bleached in the same bleaching sequence as in Example 7, the resultant bleached pulp exhibited a brightness of 69.8% which is clearly lower than that in Example 7.

When a softwood pulp was subjected to the process of the present invention, the effect of the acid treatment is lower than that for the hardwood pulp. However, as shown in Examples 8 and 9, when the unbleached softwood pulp having a Kappa number of 27.5 or the alkali-oxygen delignified softwood pulp having a Kappa number of 13.3 was acid treated under pressure generated by a compressed oxygen-containing gas, the delignification of the pulp could be significantly progressed while maintaining the pulp yield at a satisfactory level, whereas the pulp viscosity slightly decreased.

Compared with this, when the unbleached or alkali-oxygen delignified softwood pulp is acid-treated without pressurizing with the oxygen-containing gas, as shown in Comparative Examples 7 and 8, the decrease in Kappa number of the pulp due to the acid treatment is lower than that in the acid treatment with the pressurization with the oxygen-containing gas.

Accordingly, it is clear that the process of the present invention contributes to enhancing the bleachability of the unbleached pulp without decreasing the total pulp yield in the acid treatment and bleaching procedures and to significantly reducing the amounts of the bleaching chemicals necessary for the bleaching procedure.

Example 10

Mixed hardwood chips comprising 70% by weight of Japan-produced hardwood chips and 30% by weight of eucalyptus wood chips and in a bone dry weight of 500g was kraft-cooked in a laboratory indirect-heating autoclave containing a cooking liquor having an effective alkali content of 18% based on the bone dry weight of the wood chips, a degree of sulfidity of 25% and a liquor ratio of 4 to the bone dry weight of the wood chips at a cooking temperature of 160°C for a cooking time of 120 minutes. The resultant pulp was collected, and finely screened through a flat screen equipped with a 10 cuts screen plate. An unbleached hardwood kraft pulp having a Hunter brightness of 45.2%, a Kappa number of 20.1, a pulp viscosity of 23.3 mPa·s (determined in accordance with J. TAPPI, 44) was obtained in an amount of 229g in a finely screened pulp yield of 45.8%.

The unbleached pulp in a bone dry weight of 90.0g was suspended in water and added with sodium hydroxide in an amount of 1.5% based on the bone dry weight of the pulp, and diluted with ion-exchanged water to adjust the pulp consistency in the pulp slurry to 10% by weight.

The pulp slurry was placed in an indirect heating autoclave, pressurized with a commercially available compressed oxygen gas having a degree of oxygen purity of 99.9% to a pressure on gage of 5 kg/cm^2, and heated at a temperature of 100°C under the above-mentioned pressure for 60 minutes, to delignify the pulp by a medium consistency alkali-oxygen delignification method. The resultant delignified pulp was washed with ion-exchanged water and dewatered.

A delignified pulp having a Hunter brightness of 51.1%, a Kappa number of 10.2 and a pulp viscosity of 18.8 mPa·s was obtained in a bone dry weight of 88.8g.

The alkali-oxygen delignified pulp in a bone dry weight of 80.0g was suspended in water and diluted with an aqueous sulfuric acid solution prepared by dissolving concentrated sulfuric acid in ion-exchanged water and having a pH value of 2.6, to adjust the pulp consistency in the slurry to 10% by weight.

The pulp slurry was placed in a indirect heating stainless steel autoclave having a capacity of 2 liters, the inside space of the autoclave was filled with a nitrogen gas having a degree of nitrogen purity of 99.9% and pressurized with the same nitrogen gas as mentioned above to a pressure on gage of 5 kg/cm^2. The pulp slurry in the autoclave was heated at a temperature of 95°C under the above-mentioned pressure for 60 minutes, to conduct the acid treatment for the pulp. After the autoclave was cooled to room temperature, the acid-treated pulp was washed with ion-exchanged water and dewatered.

The acid treated pulp having a brightness of 51.4%, a Kappa number of 4.5 and a pulp viscosity of 17.2 mPa·s was obtained in a bone dry weight of 79.3g. In the acid treatment, the decrease in Kappa number was 55.9% and the pulp yield was 99.1%.

The acid treated pulp in a bone dry weight of 70.0g was placed in a plastic resin bag and suspended in a pulp consistency of 10% by weight in ion-exchanged water, then chlorine dioxide is added in an amount of 0.41% based on the bone dry weight of the pulp to the pulp slurry in the bag. The pulp slurry-containing bag was immersed in a constant temperature water bath at a temperature of 70°C for 30 minutes, to carry out a bleaching stage D1 procedure. The Dl-bleached pulp was washed with ion-exchanged water and dewatered.

The D1-bleached pulp was placed in a plastic resin bag and suspended in a pulp consistency of 10% by weight in ion-exchanged water. Then, sodium hydroxide was added in an amount of 1.7 times the amount of chlorine dioxide used in the D1 stage to the pulp slurry. The resultant pulp slurry was treated with the sodium hydroxide at a temperature of 70°C for 120 minutes in the same manner as in the D1 stage, to carry out an extraction procedure in an E stage. The resultant pulp after the E stage was washed with ion-exchanged water and dewatered.

The E stage-extracted pulp was placed in a plastic resin bag and suspended in a pulp consistency of 10% by weight in ion-exchanged water. Then, chlorine dioxide was added in an amount of 0.4% based on the bone dry weight of the pulp to the pulp slurry. The pulp was treated with chlorine dioxide at a temperature of 70°C for 180 minutes in the same manner as in the D1 stage to effect a D2 stage bleaching procedure. The resultant pulp was washed with ion-exchanged water and dewatered to obtain a bleached pulp in a bone dry weight of 69.2g.

The pulp yield of the multi-stage bleaching procedure was 98.9% and the total pulp yield of the acid treatment and bleaching procedures was 98.0%.

The D2 stage bleached pulp was disintegrated and then formed into a pulp sheet having a basis weight of 60 g/m^2 in accordance with TAPPI Testing Method T 205 os-71 (JIS P 8209). The pulp sheet had a brightness of 85.4% determined in accordance with JIS P 8123.

In Table 5, the Kappa number of the acid treated pulp, the decrease in Kappa number due to the acid treatment and pulp yield in the acid treatment are shown. Also, in Table 6, the amounts of the bleaching chemicals used in the D1 and D2 stages, the decrease in the total bleaching chemical consumption in the D1 and D2 stages, the decrease in bleaching chemical consumption in the E-stage in the bleaching procedure, the pulp yield of the bleaching procedure and the total pulp yield of the acid treatment and bleaching procedures are shown.

Example 11

The same acid-treated pulp having a Kappa number of 4.5 and a pulp viscosity of 17.2 mPa·s as in Example 10 was employed in a bone dry weight of 70g.

The acid treated pulp was subjected to the same D1 stage bleaching procedure as in Example 10, washed with ion-exchanged water and dehydrated.

The D1 stage bleached pulp slurry was added with sodium hydroxide in an amount of 0.69% based on the bone dry weight of the pulp and diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight. The pulp slurry was placed in an indirect heating autoclave, pressurized with a commercially available compressed oxygen gas having a degree of oxygen purity of 99.9% to a pressure on gage of 1.5 kg/cm^2, and heated at a temperature of 70°C under the above-mentioned pressure for 15 minutes. Then, the pressure of the autoclave was reduced, and the pulp slurry was heated at a temperature of 70°C under ambient atmospheric pressure (pressure on gage = O) for 105 minutes, to complete the alkali extraction (E/O) stage in the presence of oxygen for the pulp. The resultant alkali-extracted pulp was washed with ion-exchanged water and dewatered.

The alkali-extracted pulp was subjected to the same D2 stage procedure as in Example 10, except that the amount of chlorine dioxide used was changed to 0.18% based on the bone dry weight of the pulp. A bleached pulp having a Hunter brightness of 85.4% was obtained in a bone dry weight of 69.3g.

The pulp yield in the multi-stage bleaching procedure was 99.0% and the total pulp yield in the acid treatment and bleaching procedures was 98.1%.

In Table 5, the Kappa number of the acid treated pulp, the decrease in Kappa number due to the acid treatment and pulp yield in the acid treatment are shown. Also, in Table 6, the amounts of the bleaching chemicals used in the D1 and D2 stages, the decrease in the total bleaching chemical consumption in the D1 and D2 stages, the decrease in bleaching chemical consumption in the E-stage in the bleaching procedure, the pulp yield of the bleaching procedure and the total pulp yield of the acid treatment and bleaching procedures are shown.

Example 12

The same acid-treated pulp having a Kappa number of 4.5 and a pulp viscosity of 17.2 mPa·s as in Example 10 was employed in a bone dry weight of 70g.

An aqueous slurry of the acid-treated pulp was added with 1.0% of sodium hydroxide and 0.5% of hydrogen peroxide based on the bone dry weight of the pulp, diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight. The pulp slurry was placed in an indirect heating autoclave, pressurized with a commercially available compressed oxygen gas having a degree of oxygen purity of 99.9% to a pressure on gage of 1.5 kg/cm^2, and heated at a temperature of 70°C for 15 minutes. The pressure of the autoclave was reduced, and the pulp slurry was further heated at a temperature of 70°C under ambient atmospheric pressure for 105 minutes to complete an alkali extraction (E/OP) in the presence of oxygen and hydrogen peroxide. After the autoclave was cooled, the alkali extracted (E/OP) pulp was washed with ion-exchanged water and dewatered.

The E/OP alkali-extracted pulp slurry was added with 1.5% of sodium hydroxide and 3.0% of hydrogen peroxide, based on the bone dry weight of the pulp, and diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight, and placed in an indirect heating autoclave.

The pulp slurry in the autoclave was pressurized with a commercially available compressed oxygen gas having a degree of oxygen purity of 99.9% to a pressure on gage of 5 kg/cm^2 and heated at a temperature of 100°C under the above-mentioned pressure for 60 minutes, to complete a hydrogen peroxide (PO) bleaching treatment under a pressure imparted by the compressed oxygen gas.

The resultant bleached pulp was washed with ion-exchanged water and dewatered.

The resultant bleached pulp in a bone dry weight of 68.8g had a brightness of 84.2% and a pulp viscosity of 14.8 mPa·s. The pulp yield in the bleaching procedure was 98.3%.

Table 7 shows the brightness and pulp viscosity of the bleached pulp, and the total pulp yield in the acid treatment and bleaching procedures.

Example 13

The same acid-treated pulp having a Kappa number of 4.5 and a pulp viscosity of 17.2 mPa·s as in Example 10 was employed in a bone dry weight of 70g.

The acid treated pulp slurry was added with sodium hydroxide in an amount of 1.5% and hydrogen peroxide in an amount of 2.0% based on the bone dry weight of the pulp and diluted with ion-exchanged water to adjust the pulp consistency in the slurry to 10% by weight. The pulp slurry was placed in an indirect heating autoclave, pressurized with a commercially available compressed oxygen gas having a degree of oxygen purity of 99.9% to a pressure on gage of 5 kg/cm^2, and heated at a temperature of 100°C under the above-mentioned pressure for 60 minutes, to complete the hydrogen peroxide (PO) bleaching procedure under a pressure imparted by the oxygen gas. The resultant pulp was washed with ion-exchanged water and dewatered.

The resultant semi-bleached pulp in a bone dry weight of 69.5g had a brightness of 72.8% and a pulp viscosity of 15.7 mPa·s. The pulp yield in the bleaching procedure was 99.3%.

Table 7 shows the brightness and pulp viscosity of the semi-bleached pulp and the total pulp yield in the acid treatment and bleaching procedures.

Comparative Example 9

The same acid treatment and multi-stage bleaching procedures (D1-E-D2) as in Example 10 were carried out, except that the acid treatment was carried out in a nitrogen gas atmosphere under ambient atmospheric pressure (no pressurization was applied), the amount of the bleaching chemical used in the D1 stage was changed to 0.65% based on the bone dry weight of the pulp.

A bleached pulp having a brightness of 85.3% was obtained in a bone dry weight of 69.lg.

The Kappa number of the acid-treated pulp was 6.5, the decrease in Kappa number due to the acid treatment was 36.3%, the pulp viscosity of the acid-treated pulp was 17.2 mPa·s, the bone dry weight of the acid treated pulp was 79.5g, and the pulp yield in the acid treatment was 99.4%.

In the multi-stage bleaching procedure, the bone dry weight of the bleached pulp was 69.lg, the pulp yield in the bleaching procedure was 98.7% and the total pulp yield in the acid treatment and bleaching procedures was 98.1%. Table 5 shows the Kappa number of the acid-treated pulp, the decrease in Kappa number due to the acid-treatment and the pulp yield in the acid treatment. Also, Table 6 shows the amounts of the bleaching chemical in the D1 and D2 stages, the decrease in the bleaching chemical consumption in the D1 and D stages, the decrease in the bleaching chemical consumption in the E stage, the pulp yield in the bleaching procedure and the total pulp yield in the acid treatment and bleaching procedures.

Comparative Example 10

The same procedures as in Comparative Example 5 were carried out to produce a bleached pulp.

The resultant bleached pulp had a bone dry weight of 68.9g, a brightness of 81.4%, a pulp yield in the bleaching procedure of 98.4% and a pulp viscosity of 14.1 mPa·s.

Table 7 shows the brightness and pulp viscosity of the bleached pulp, and the total pulp yield in the acid treatment and the bleaching procedures.

Comparative Example 11

A semi-bleached pulp was produced by the same procedures as in Comparative Example 6.

The semi-bleached pulp had a bone dry weight of 69.5g, a brightness of 69.8%, a pulp yield of 99.3% and a pulp viscosity of 15.1 mPa·s.

Table 7 shows the brightness and pulp viscosity of the semi-bleached pulp and the total pulp yield in the acid treatment and bleaching procedures.

Table 5

Item / Example No.		Unbleached non-acid treated pulp		Unbleached, acid-treated pulp			
		Kappa number	Pulp viscosity (mPa·s)	Kappa number	Decrease in Kappa number (%)	Pulp viscosity (mPa·s)	Pulp yield (%)
Example	10	10.2	18.8	4.5	55.9	17.2	99.1
	11			4.5	55.9	17.2	99.1
	12			4.5	55.9	17.2	99.1
	13			4.5	55.9	17.2	99.1
Comparative Example	9			6.5	36.3	17.2	99.4

Table 6

Item / Example No.		Multi-stage (D1-E-D2) bleaching procedure					Total pulp yield in acid treatment and bleaching (%)
		Amount of bleaching chemical used		Decrease in bleaching chemical consumption (%)		Pulp yield (%)	
		D1-stage	D2-stage	D1 + D2 stages	E-stage		
Example	10	0.41	0.4	38.6	55.4	98.9	98.0
	11	0.41	0.18	55.3	55.4	99.0	98.1
Comparative Example	9	0.65	0.4	20.5	29.3	98.7	98.1

Table 7

Item / Example No.		Acid-treated, bleached pulp		
		Brightness (%)	Pulp viscosity of bleached pulp (mPa·s)	Total pulp yield in acid treatment and bleaching (%)
Example	12	84.2	14.8	97.4
	13	72.8	15.7	98.4
Comparative Example	10	81.4	14.1	97.7
	11	69.8	15.1	98.6

In Tables 5 to 7, Examples 10 to 13 show that when an alkali-oxygen delignified pulp having a Kappa number of 10.2 was acid treated under a pressure imparted by a compressed nitrogen-containing gas, the acid treatment under the nitrogen-containing gas pressure enables the delignification of the pulp fibers to be greatly promoted while minimizing the decrease in the pulp viscosity (corresponding to the degree of polymerization), and the bleaching procedure to be easily carried out to obtain a bleached pulp having a desired brightness at a satisfactory pulp yield, while decreasing the bleaching chemical consumption.

Also, Example 11 shows that the acid-treated pulp produced under a nitrogen-containing gas pressure caused the delignification effect on the pulp by the alkali-extraction (E/O) stage in the presence of oxygen to be promoted and thus the amount of the bleaching chemicals necessary to obtain a pulp having a desired brightness could be reduced to a great extent.

Example 12 shows that in the process of the present invention, the acid treatment under the nitrogen-containing gas pressure enabled the alkali-oxygen delignified pulp to be bleached to a desired pulp brightness of, for example, 84.2%, without using chlorine or a chlorine-containing chemical in a bleaching sequence, for example, E/op-PO. However, when the acid treatment was carried out without pressurization with the nitrogen-containing gas, and the resultant acid-treated pulp was subjected to the same chlorine-free bleaching procedure as in Example 12, the resultant bleached pulp an unsatisfactory brightness, for example, of 81.4% as shown in Comparative Example 10.

Further, when the acid treatment of the pulp is carried out in a nitrogen gas atmosphere without pressurization, or using no nitrogen gas as in Comparative Examples 3, 4 and 9 to 11, the decrease in Kappa number in the acid treated is small, for example, 36%, in comparison with that in the acid treatment under the nitrogen-containing gas pressure, the decrease in the bleaching chemical consumption in the bleaching procedure is low as shown in Comparative Examples 3 and 9, and even when the alkali-extraction (E/O) step in the pressure of oxygen is inserted into the bleaching procedure, a significant decrease in the bleaching chemical consumption could not be attained as shown in Comparative Example 4.

The acid-treated pulp prepared in the process of the present invention could be converted to a semi-bleached pulp having a brightness of 72.8% as shown in Example 13, by a hydrogen peroxide-bleaching under an oxygen-containing gas pressure. However, as shown in Comparative Example 11, the acid treatment in which the pressurization with the compressed nitrogen-containing gas is not applied, resulted in a bleached pulp having a low level of brightness of 69.8%, even when the bleaching procedure is carried out in the same bleaching sequence as in Example 13.

Namely, in the process of the present invention, when the acid treatment for the unbleached pulp is carried out under a nitrogen-containing gas pressure before the bleaching procedure, the amount of the bleaching chemicals necessary to obtain a bleached pulp having a desired brightness can be reduced without decreasing the total pulp yield in the acid treatment and bleaching procedures and the pulp viscosity of the bleached pulp.

Claims

1. A process for producing a bleached pulp, comprising the steps of:

    pulping a wood material to produce an unbleached pulp; and
    bleaching the unbleached pulp with a bleaching chemical in at least one stage

wherein before the bleaching step with the bleaching chemical, the unbleached pulp is treated with a aqueous acid solution in a gas containing at least one member selected form the group consisting of oxygen and nitrogen under pressure.

2. The process as claimed in claim 1, wherein before the acid treating step, the unbleached pulp is delignified with oxygen in an aqueous alkali solution and then the acid treatment of the delignified pulp is carried out in an oxygen-containing gas under pressure.

3. The process as claimed in claim 2, wherein the acid treatment of the alkali-oxygen delignified pulp is carried out in a consistency of the pup of 5 to 40% by weight, at a pH value of the aqueous acid solution of 2 to 6 at a temperature of 50 to 150°C under a pressure on gage of the oxygen-containing gas of 0.5 to 9.0 kg/cm^2 for 5 to 120 minutes.

4. The process as claimed in claim 2, wherein oxygen-containing gas contains 20% by volume or more of oxygen.

5. The process as claimed in claim 2, wherein a waste water discharged from the acid treating step under pressure is recovered.

6. The process as claimed in claim 1, wherein the bleaching chemical contains no chlorine.

7. The process as claimed in claim 1, wherein the bleaching chemical contains no chlorine and no chlorine-containing bleaching compound.

8. The process as claimed in claim 1, wherein waste water from the acid treating step and waste water from the bleaching step with the bleaching chemical are recovered.

9. The process as claimed in claim 1, wherein the bleaching step with the bleaching chemical includes at least one extraction procedure of the acid-treated pulp with an alkali extraction liquor containing at least one member selected from the group consisting of oxygen and hydrogen peroxide.

10. The process as claimed in claim 1, wherein before the acid treating step, the unbleached pulp is delignified with oxygen in an aqueous alkali solution and then the acid treatment of the alkali-oxygen delignified pulp is carried out in an nitrogen-containing gas under pressure.

11. The process as claimed in claim 10, wherein the acid treating step of the delignified pulp is carried out in a consistency of the pulp of 5 to 40% by weight at a pH value of the aqueous acid solution of 2 to 6 at a temperature of 50 to 150°C under a pressure on gage of the nitrogen-containing gas of 0.5 to 9.0 kg/cm^2 for 5 to 120 minutes.

12. The process as claimed in claim 10, wherein the nitrogen-containing gas for the acid treating step comprises a by-product gas delivered from a procedure in which a oxygen gas for the delignifying step with oxygen in an aqueous alkali solution is concentrate-collected from air.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 66 0014

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 95 08021 A (KAMYR INC) 23 March 1995 * page 8, line 6 - line 12; figure 1B * ---	1-3,5-9	D21C9/10
X	DE 34 46 301 A (DEGUSSA) 19 June 1986 * page 4, line 20 - line 28 * ---	1	
A	WO 96 25552 A (A. AHLSTROM CORP) 22 August 1996 * page 10, line 26 - page 11, line 10 * * page 5, line 1 - line 16 * -----	1-4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 July 1998	Bernardo Noriega, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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