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## (54) PULP BLEACHING PROCESSES

(57) The present invention aims to further advance the acid treatment or irradiation technology for pulp to develop a bleaching process using smaller amounts of chlorine chemicals with higher efficiency as compared with conventional bleaching processes. It also aims to provide an excellent high brightness pulp having a low environmental impact and no discoloration as well as a paper containing it.

The present invention provides a chlorine-free bleaching process with very high efficiency by irradiating a pulp washed after an acid treatment with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions, preferably in a pH range of 10 - 13. The acid treatment can be performed under conditions of pH 1 - 6 and a temperature of 80°C or more. The irradiation treatment can be performed in the presence of at least one compound selected from the group consisting of reducing agents, peroxides, and hydrogen-donating organic compounds.

The present invention also provides a high brightness chemical pulp having an ISO brightness of 88% or more and a brightness loss of 1.0% or less in a specific fading test.

Pulp after irradiation reaction

Pulp after irradiation reaction

Interest by after irradiation reaction

It reaction 1

It reaction 2 (recycled to at irradiation reaction)

It reaction 2 (recycled to at irradiation treaction)

It reaction 1

One of the irradiation treaction

One of the irradiation reaction

It reaction 1

One of the irradiation reaction

One of the irradiation reaction 1

It reaction 1

It

Figure 1

#### **Description**

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#### **TECHNICAL FIELD**

[0001] The present invention relates to a bleaching process for pulp characterized in that a pulp washed after an acid treatment is irradiated with UV light and/or visible light under alkaline conditions; a bleaching process characterized in that a pulp washed after an acid treatment is treated by a combination of irradiation with UV light and/or visible light and ozone feeding, thereby promoting pulp bleaching; and a bleaching process for chemical pulp by which a high brightness chemical pulp can be obtained (herein collectively referred to as the first invention); as well as a high brightness chemical pulp with greatly improved discoloration and a paper containing it, more specifically a novel high brightness chemical pulp with greatly improved discoloration obtained by further treating a bleached chemical pulp with UV light and a paper containing it (herein collectively referred to as the second invention).

#### **BACKGROUND ART**

[0002] The background art of the first invention described below is as follows.

[0003] To meet the growing concern about the influence of waste from bleaching processes of paper pulp plants on the environment, chlorine-free (ECF) bleaching or even totally chlorine-free (TCF) bleaching is becoming global and mainstream in place of conventional bleaching techniques mainly using chlorine or chlorine-based chemicals or combinations thereof. Under such circumstances, there is a tendency to use limited chemicals such as chlorine dioxide, hydrogen peroxide, oxygen and ozone in ECF bleaching or TCF bleaching. However, pulp quality, especially brightness obtained by bleaching with only such chemicals is limited even if they are used in combination, or large amounts of expensive chemicals must be used to attain sufficient quality. It would be desirable to develop chlorine-free chemicals having unprecedentedly excellent bleaching performance or novel bleaching techniques to solve these problems.

[0004] It has been known that various metals from pulp promote decomposition of oxygen-based bleaching chemicals, thereby wasting the oxygen-based bleaching chemicals. Thus, techniques for removing these metals to improve the bleaching efficiency of oxygen-based bleaching chemicals were proposed, such as acid treatments at relatively low temperatures or chelator treatments or combinations thereof. Such acid treatment techniques previously disclosed include a process for delignifying a pulp prepared from a lignocellulose material by oxygen bleaching, comprising first adding a nitrite and an acid to the pulp to pretreat the pulp, followed by oxygen bleaching, or a bleaching process comprising subjecting a cooked chemical pulp to an acid treatment followed by delignification with a peroxide and pressurized oxygen in an alkaline medium (e.g., patent document 1, patent document 2). Another bleaching process was also disclosed, comprising subjecting a cooked chemical pulp to an oxygen bleaching treatment at high temperature and high pressure and then an acid treatment or a chelator treatment followed by delignification/bleaching with a peroxide or hydrogen peroxide and oxygen in an alkaline medium (e.g., patent document 3).

**[0005]** It has become known from recent findings that not only lignin and modified lignin but also hexenuronic acid are responsible for discoloration of ECF or TCF bleached pulp. This hexenuronic acid is produced by demethylation from methylglucuronic acid in hemicellulose during the cooking process. This hexenuronic acid is said to be responsible for discoloration of the pulp. A method proposed to remove the hexenuronic acid was an acid treatment technique carried out at a relatively high temperature. This method comprises treating unbleached pulp at a high temperature under acid conditions, thereby acid-hydrolyzing the hexenuronic acid and modified lignin to remove them. For example, a technique was disclosed wherein a suspension of a cellulose pulp prepared by the sulfate process or alkaline process is heated and treated at about 85 to 150°C and a pH of about 2 to 5 to remove at least about 50% of hexenuronic acid in the cellulose pulp, thereby decreasing the Kappa number of the pulp by 2 to 9 units (see patent document 4).

**[0006]** Bleaching techniques using irradiation were also disclosed, such as techniques involving UV irradiation in hydrogen peroxide bleaching of unbleached kraft pulps (e.g., see non-patent document 1, or patent document 5), or UV irradiation in oxygen bleaching of unbleached kraft pulps (e.g., see non-patent document 2). UV irradiation in the presence of a peroxide as a pretreatment for promoting normal alkaline hydrogen peroxide bleaching was also disclosed (e.g., see patent document 6).

**[0007]** Other disclosed techniques include a pulp bleaching process using a reducing agent involving irradiation with UV light or visible light or a combination thereof (see patent document 7), or a process involving irradiation with UV light or visible light or a combination thereof in the presence of an organic peroxide represented by ROOR' as an oxidizing agent (see patent document 8).

**[0008]** Recently, water pollution caused by industrial wastewater or domestic wastewater is worsening and water environment pollution has become social concerns. Under such circumstances, water environment protection technologies such as activated carbon treatment, membrane treatment, ozone treatment, UV treatment, biological treatment, etc. are under active development. Among them, the advanced oxidation technology combining ozone and UV light (see patent document 9) is a promising comprehensive treatment capable of improving efficiency of decomposition and

deodorizing, effects of decoloring and sterilizing as well as ensuring clarification treatment without producing secondary waste.

Patent document 1: Japanese Patent No. 2895977.

5 Patent document 2: JPA No. Hei 6-101186.

Patent document 3: JPA No. Hei 6-158573.

Patent document 4: JPA No. Hei 10-508346.

Patent document 5: JPA No. 2002-88673.

Patent document 6: JPA No. Hei 6-128890.

Patent document 7: JPA No. 2002-88671.

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Patent document 8: JPA No. 2002-88672.

Patent document 9: JPA No. 2004-97992.

Non-patent document 1: B. Marccia, et al. J34 - J39, JOURNAL OF PULP AND PAPER SCIENCE: Vol. 17, No. 2, March 1991.

Non-patent document 2: J.Abbot, et al. p198 - 202, Appita Vol. 46, No. 3, May 1993.

The background art of the second invention described below is as follows.

[0009] Paper products mainly made from chemical pulp, especially communication papers such as inkjet papers and thermal transfer papers or photographic base papers are required to have high brightness. Normally, in order to increase brightness of unbleached kraft pulp, materials responsible for coloration such as lignin or polysaccharides remaining in the unbleached pulp are removed by multistage bleaching with chemicals such as chlorine, hypochlorites, chlorine dioxide, oxygen, hydrogen peroxide, ozone, etc. The ISO brightness of pulp obtained by chlorine bleaching with chlorine gas or more environmentally friendly ECF bleaching with reduced production of organic chlorine compounds using chlorine dioxide is normally 82 - 86%. High brightness pulp bleached to a higher brightness level than normal is typically prepared by applying harsher cooking and/or bleaching conditions or by using easy-to-cook and bleach wood species having low contents of phenolic extract components.

[0010] As a prior technique for preparing high brightness pulp, a process for preparing a high brightness pulp was disclosed, for example, characterized in that a pulp bleached in a sequence including at least one chlorine bleaching stage is treated with xylanase and further bleached in a bleaching sequence including a hypochlorite stage and a chlorine dioxide stage (see patent document 10). Another process for preparing a high brightness pulp was disclosed, comprising further bleaching a bleached pulp derived from a lignocellulose material via a continuous sequence of a hypochlorite bleaching stage under high temperature and highly alkaline conditions and a chlorine dioxide bleaching stage, characterized in that the chlorine dioxide bleaching stage is performed at a chlorine dioxide concentration of 1-3% by weight (on the basis of the bone dry weight of the pulp) at a high temperature of 91°C or more and less than 100°C (see patent document 11). A photographic base paper was also disclosed, characterized in that it uses a chemical pulp bleached in a bleaching sequence of oxygen bleaching - ozone bleaching - alkali extraction - hydrogen peroxide bleaching chlorine dioxide bleaching - hydrogen peroxide bleaching - chlorine dioxide bleaching and that the chemical pulp is bleached with 0.1 - 1.0% by weight of ozone on the basis of the bone dry weight of the pulp during the ozone bleaching stage (see patent document 12). A process for preparing a high brightness pulp with improved discoloration for use in photosensitive materials was also disclosed, characterized in that an unbleached kraft pulp having a kappa number of 23 or less is bleached with oxygen at a delignification degree of 40% or more and then bleached with oxone at a pulp consistency of 25% or more and then adjusted to a PN number of 2.8 or less followed by multistage bleaching including hydrogen peroxide bleaching and chlorine dioxide bleaching (see patent document 13). However, it was difficult to avoid brightness loss with time or so-called discoloration phenomenon in high brightness pulps obtained by the conventional processes because very small amounts of potential coloring matters liable to be darkened by heat or UV light remain in them.

Patent document 10: JPA No. Hei 6-101185.

Patent document 11: JPA No. Hei 9-105091.

Patent document 12: JPA No. 2002-62622.

Patent document 13: JPA No. 2003-41494.

DISCLOSURE OF THE INVENTION

#### PROBLEMS TO BE SOLVED BY THE INVENTION

**[0011]** The first invention aims to further advance the acid treatment or irradiation technology for pulp as described above to develop a bleaching process using less chlorine chemicals with higher efficiency as compared with conventional

bleaching processes, and to develop a TCF bleaching process capable of achieving a final ISO brightness of 84% or more while greatly shortening the irradiation period at the light bleaching stage by inserting an acid treatment and a bleaching stage used in normal TCF bleaching before the light bleaching stage and an alkaline hydrogen peroxide bleaching stage after the light bleaching stage.

[0012] The second invention aims to overcome the drawbacks of the conventional technology and to provide a high brightness pulp having a low environmental impact and no discoloration as well as a paper containing it.

#### MEANS TO SOLVE THE PROBLEMS

[0013] As a result of careful studies, we found a chlorine-free bleaching process with very high efficiency by irradiating a pulp washed after an acid treatment with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions, preferably in a pH range of 10 - 13, and accomplished a first aspect of the first invention.

**[0014]** We also found a pulp bleaching process with very high efficiency by irradiating a pulp, that is washed after an acid treatment, with UV light and/or visible light at a wavelength of 100 - 400 nm in the presence of ozone, and accomplished a second aspect of the first invention.

**[0015]** We also found a very efficient totally chlorine-free (TCF) pulp bleaching process wherein an oxygen-delignified pulp is acid-treated and then bleached by a bleaching process used in normal TCF bleaching, and the resulting pulp is further subjected to a light bleaching treatment with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions, followed by alkaline hydrogen peroxide bleaching (a third aspect of the first invention).

As a result of careful studies to overcome the drawbacks of conventional technology and to attain a pulp with such a high brightness and low discoloration, we found that a pulp having high brightness and no discoloration as described above and also having high paper strength can be prepared by further treating a bleached pulp with UV light, and accomplished the second invention. Accordingly, the second invention relates to a high brightness chemical pulp having an ISO brightness of 88% or more and a brightness loss of 1.0% or less in the following fading test:

a hand-made paper is prepared according to JIS P 8222 and irradiated with a xenon lamp at an intensity of 67 W/m<sup>2</sup> for 30 minutes in an atmosphere at 30°C according to fading test method B of J. TAPPI No.21 Paper and Paperboard (using a xenon arc lamp light fastness tester) and then the ISO brightness is measured and a loss from the ISO brightness before treatment is determined.

#### BRIEF EXPLANATION OF THE DRAWINGS

#### [0016]

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Figure 1 shows an example of a system using an irradiation reactor in the present invention.

Figure 2 shows an irradiation reactor with an internal light source used in the present invention.

Figure 3 shows an irradiation reactor with an internal light source used in the examples of the present invention.

Figure 4 shows the relationship between pH and brightness in irradiation treatments using a hardwood pulp.

Figure 5 shows the relationship between irradiation period and brightness in irradiation treatments using a hardwood pulp.

Figure 6 shows the relationship between pH and brightness in irradiation treatments using a softwood pulp.

Figure 7 shows an example of an experimental apparatus for UV bleaching test.

#### REFERENCE NUMERALS

#### [0017]

10: irradiation target material conditioning	tank;
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11: irradiation reactor feeding pump;

50 12: irradiation reactor;

20: irradiation reaction chamber;

21: quartz glass tube;22: irradiation source;

23a, 23b: three-way valve; 24: diffuser, diffuser tube;

25: pulp slurry inlet;

26: pulp slurry outlet;27: stirrer.

#### PREFERRED EMBODIMENTS OF THE INVENTION

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[0018] Embodiments of the first invention are explained below.

[0019] The first and second aspects of the first invention are applied to pulps washed after an acid treatment. Especially, they are applied to kraft pulps (KPs) and are well suitable for not only unbleached KPs but also oxygen-delignified KPs, ozone-bleached KPs, etc. The bleaching process according to the third aspect of the first invention is applied to kraft-cooked and oxygen-delignified chemical pulps. The pulp materials used in the first invention and the second invention (chemical pulp) are not specifically limited and include hardwood and softwood as well as other plants such as kenaf, flax, rice, bagasse, bamboo, etc. In the pulp bleaching process according to the second aspect of the first invention, the oxygen-delignified pulp is acid-treated and then bleached by a bleaching process used in normal TCF bleaching, and the resulting pulp is further subjected to an irradiation treatment with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions, followed by alkaline hydrogen peroxide bleaching.

**[0020]** The type of the acid used in the acid treatment of the present invention may be inorganic or organic. Inorganic acids that can be used include mineral acids such as sulfuric acid, hydrochloric acid, nitric acid, sulfurous acid, nitrous acid, phosphoric acid, and residual acids in chlorine dioxide generators. Sulfuric acid is preferred. Organic acids that can be used include acetic acid, lactic acid, oxalic acid, citric acid, formic acid, etc. The pH during the acid treatment is in the range of 1.0 - 6.0, preferably 1.0 - 5.0, more preferably 2.0 - 5.0, most preferably 2.5 - 3.5. If the pH is less than 1.0, hexenuronic acid or the like and metal ions are sufficiently removed, but the viscosity greatly decreases because of excessive acidity. If the pH exceeds 6.0, however, the acid concentration is so low that hexenuronic acid or the like and metal ions are insufficiently removed. Hardwood pulps rich in hexenuronic acid can be acid-treated at lower temperatures in a pH range of 2.5 - 3.5, which leads to the advantage that the acid treatment cost can be reduced.

**[0021]** The acid treatment can be performed at an atmospheric pressure or under pressure and at a temperature of 80°C - 180°C, preferably 80°C - 130°C. Temperatures of 30 °C or higher and lower than 80°C are effective for removing metals but not effective for removing hexenuronic acid or the like. Temperatures lower than 100°C are advantageous in terms of equipment costs because no pressure-tight reaction chamber is required.

**[0022]** The pulp consistency during the acid treatment is in the range of 0.1 - 50% by weight, preferably 1.0 - 30% by weight, more preferably 2.0 - 20% by weight.

**[0023]** The extent to which hexenuronic acid or the like and harmful metals are removed depends on the pH, reaction temperature and reaction period during the acid treatment. Thus, the reaction period is determined as appropriate depending on the other two conditions, but typically the reaction period is 1.5 - 6 hours at a reaction temperature of 90°C, the reaction period is 50 minutes - 5 hours at a reaction temperature of 95°C, the reaction period is 30 minutes - 4.5 hours at a reaction temperature of 100°C, and the reaction period is 5 - 50 minutes at a reaction temperature of 120 - 130°C.

**[0024]** Ozone bleaching under acidic conditions is also a form of the acid treatment contemplated by the present invention, and normal acidic ozone bleaching conditions can be applied. In this connection, typical acidic ozone bleaching conditions regarded as suitable include using ozone gas at an ozone concentration of 1 - 20% by weight at pH 1.0 - 8.0 (the first and third aspects of the first invention) or pH 1 - 7(the second aspect of the first invention) at a pulp consistency of 0.1 - 50% by weight and a temperature of 25 - 95°C. The pressure here is not specifically limited from a negative pressure state to a pressurized state.

**[0025]** A further greater bleaching reaction promoting effect is obtained in the irradiation treatment by using chelating agents such as EDTA, DPTA in combination with the acid treatment.

**[0026]** Although the reason why the acid treatment promotes the bleaching effect in the subsequent irradiation treatment with UV light and/or visible light is not clear, lignin and metal ions, especially iron ions remaining in pulp form metal complexes, which become colored by the irradiation treatment. Thus, it is assumed that the bleaching effect of the irradiation treatment is improved by removing metal ions by the acid treatment.

**[0027]** In the present invention, the pulp can be dehydrated and/or washed by using a known dehydrator and/or washing after the acid treatment including ozone bleaching. Washing can be performed by using not only fresh water but also wastewater generated from bleaching processes after the acid treatment or wastewater generated from papermaking processes.

[0028] In the present invention, the acid-treated pulp is irradiated with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions, preferably at pH 10 - 13. Especially, hardwood pulps are preferably treated at pH 10 - 12, and softwood pulps are treated at pH 11 - 13. In the second aspect of the first invention, the acid-treated pulp is irradiated with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions or acidic conditions. Preferably, the alkaline conditions are in a pH range of 10 - 13 and the acidic conditions are in a pH range of 2 - 4. The alkalis used for this pH adjustment can be normal alkaline chemicals, but especially preferred are sodium hydroxide, potassium hydroxide, sodium silicate and sodium carbonate because of easy handling.

**[0029]** The pulp consistency during the irradiation treatment according to the present invention is preferably 0.1 - 12% by weight. Consistencies lower than 0.1% by weight are not preferred because energy efficiency decreases though

bleaching reaction efficiency increases. Consistencies higher than 12% by weight are not preferred because the rheology of pulp slurry in the irradiator decreases so that bleaching reaction efficiency decreases.

**[0030]** The temperature of pulp slurry during this irradiation treatment is preferably 20 - 95°C, and temperatures lower than 20 °C are not preferred because bleaching reaction efficiency is low while temperatures exceeding 95°C are not preferred, either, because pulp quality may deteriorate or the pressure in the reactor may exceed atmospheric pressure so that the reactor must be designed to resist pressure.

**[0031]** The wavelength of the light emitted in the irradiator of the present invention is preferably 100 - 400 nm, especially 200 - 360 nm (180 - 360 nm in the second aspect of the first invention). Wavelengths shorter than 100 nm are not preferred because photodegradation of cellulose is promoted so that pulp strength is greatly lowered, while wavelengths exceeding 400 nm are not preferred, either, because photosensitive coloring matters are insufficiently photoexcited so that light bleaching performance is greatly lowered.

**[0032]** Irradiation sources that can be used include those emitting light in a wavelength range of 100 - 400 nm, specifically xenon short arc lamps, ultra high pressure mercury lamps, high pressure mercury lamps, low pressure mercury lamps, deuterium lamps, metal halide lamps, etc., [see Kinoshita: "UV irradiators", Adhesion (2002, vol. 46, No. 7) pp. 20 - 27; or Sugimori Akira: "Photochemistry, Chapter 8 Experimental methods of photochemistry I" (Shokabo Publishing Co., Ltd. 1998) pp. 126-136], which can be used alone or by combining two or more methods.

**[0033]** The degree of irradiation to which pulp is exposed in the irradiation reactor can be adjusted at will by controlling the retention time of pulp in the irradiation reactor or controlling the power of the irradiation source. Specifically, the retention time of pulp in the irradiation reactor can be controlled by diluting the pulp consistency in the irradiation reactor with water or by blowing air or an inert gas such as nitrogen into pulp slurry to control the pulp consistency. These conditions can be selected as appropriate depending on the pulp quality goals (brightness, etc.) after the irradiation reaction.

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[0034] The second aspect of the first invention is characterized in that the irradiation treatment with UV light and/or visible light at a wavelength of 100 - 400 nm is performed in the presence of ozone. In the case of irradiation with light in a wavelength range of 135 - 242 nm, ozone is normally generated due to the presence of air in the gas layer around the light source. In the present invention, air is continuously supplied to the surroundings of the light source while continuously extracting the generated ozone and injecting it into the irradiation target material, whereby the ozone can be used as a reaction promoter without supplying ozone from any external source. In addition, a larger amount of ozone can be obtained by supplying air to the gas layer around the light source. Naturally, the generated ozone can be used not only as a promoter during the irradiation reaction but also for regular ozone bleaching. Thus, another great advantage of the present invention is that the ozone by-produced in the irradiation reactor can be used. Ozone can also be generated by supplying such air or oxygen to the pulp to be treated but not to the surroundings of the light source. Moreover, ozone obtained from an external source by a method not relying on such effect of UV light can also be used as a reaction promoter.

[0035] The concentration of the ozone by-produced in the irradiation reactor is 0.5 - 100 ppm, depending on the manner of supplying air or oxygen or the concentration of oxygen. A major feature of the second aspect of the first invention is that a high bleaching efficiency can be obtained with even such low-concentration ozone by combination with the irradiation treatment.

**[0036]** This concept can be further expanded to select and use multiple light sources having a characteristic wavelength range within 100 - 400 nm and different characteristic wavelengths as light sources in the irradiation reactor. Specifically, a light source having a narrow wavelength characteristic of 135 - 242 nm providing a high ozone-generating efficiency and a light source having an evenly distributed wavelength range of 100 - 400 nm suitable for irradiation reaction can be combined, for example, whereby a further higher bleaching efficiency can be obtained.

**[0037]** In the irradiation treatment of the present invention, the irradiation reaction efficiency can be increased by using a combination of additives such as reducing agents (e.g., NaBH<sub>4</sub>, hydrazine, hydrogen), oxidizing agents (e.g., oxygen, ozone), peroxides (e.g., hydrogen peroxide, peracetic acid, Na percarbonate, Na perborate), hydrogen-donating organic compounds (e.g., alcohols; linear amines such as ethyl amine, diethylamine; cyclic amines such as tetramethyl piperidine), acetyl-containing organic compounds (e.g., a-acetyl-γ-butyrolactone, acetol, acetone).

[0038] In the third aspect of the first invention, ozone bleaching, hydrogen peroxide bleaching and the like can be used alone or in combination as TCF bleaching for attaining an ISO brightness of 70 - 75% before the light bleaching stage.

[0039] In the third aspect of the first invention, ozone bleaching can be performed under normal ozone bleaching conditions. That is, ozone bleaching conditions may include using ozone gas at an ozone concentration of 1 - 20% by

weight at pH 1 - 8, a pulp consistency of 0.1 - 50% by weight, and a temperature of 25 - 95°C. The pressure during ozone bleaching is not specifically limited from a negative pressure state to a pressurized state.

**[0040]** In the third aspect of the first invention, hydrogen peroxide bleaching can be performed under normal alkaline hydrogen peroxide bleaching. That is, alkaline hydrogen peroxide bleaching can be performed with hydrogen peroxide at a concentration of 0.1 - 2.0% by weight based on the pulp, pH 11 - 13, a pulp consistency of 0.1 - 50% by weight, and a temperature of 50 - 95°C.

[0041] In the third aspect of the first invention, the ISO brightness has been improved to 70 - 75% in advance by

normal TCF bleaching after the acid treatment, whereby the treatment period for light bleaching can be greatly shortened, and as a result, electric power costs required for light bleaching can be greatly reduced. Moreover, the ISO brightness is improved by 5% or more to reach 75 - 80% by light bleaching followed by hydrogen peroxide bleaching at the final bleaching stage, whereby the hydrogen peroxide bleaching reaction is promoted so that a pulp having an ISO brightness of 84% or more can be efficiently obtained. In terms of bleaching costs and pulp quality, it is not preferable to increase the brightness over 75% by TCF bleaching before light bleaching because larger amounts of chemicals are required under harsher reaction conditions (high temperature, long period). If the ISO brightness before light bleaching is higher than 80%, only very small amounts of coloring components are contained in the pulp so that the reaction efficiency of light bleaching significantly deteriorates. Thus, the brightness is preferably improved by hydrogen peroxide bleaching rather than light bleaching in terms of bleaching costs. If the brightness after TCF bleaching is lower than 70%, large amounts of coloring components are contained in the pulp so that a long period is required for the light bleaching treatment to achieve a final brightness of 84% or more, which invites an increase in electric power costs. If the brightness after light bleaching is lower than 75%, it is difficult to achieve a final brightness of 84% or more by hydrogen peroxide bleaching alone because of relatively large amounts of hard-to-bleach coloring components remaining in the pulp.

[0042] An example of a system using an irradiation reactor in the present invention is shown in Figure 1.

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[0043] An acid-treated pulp is received in an irradiation target material conditioning tank (10), where it is conditioned to a temperature, pH and pulp consistency suitable for irradiation reaction while stirring. The conditioned irradiation target material 1 is sent to an irradiation reactor (12) via an irradiation reactor feeding pump (11). Before that, an additive such as a reducing agent in the irradiation reaction is added as a chemical solution, if desired. The additive can be added at the site indicated in Figure 1 or the irradiation target material conditioning tank (10) or both at will depending on the properties of the additive or irradiation reaction conditions, but fast-reacting additives or highly decomposable additives are preferably added immediately before the entry into the irradiation reactor (12), i.e. the site indicated in Figure 1.

**[0044]** If desired, a gas can be supplied before the entry into the irradiation reactor (12). This allows the pulp consistency in the irradiation reactor (12) to be controlled (in terms of% by volume here because of the low gas density), whereby the retention time of the pulp in the irradiation reactor (12) or the irradiation reaction period can be controlled at will. The type of the gas used here is preferably air or an inert gas such as nitrogen, and such gas is used as fine bubbles dispersed in a pulp slurry. When a gas such as hydrogen, oxygen or ozone is used among photoreaction promoters, it can also be supplied to a site indicated in the figure in the same manner.

**[0045]** Then, the pulp having reached quality goals and leaving the irradiation reactor (12) after the irradiation reaction exits the irradiation reaction and is sent to the subsequent step (C1: pulp after irradiation reaction 1). The pulp falling short of pulp quality goals is recycled to repeat the irradiation reaction (C2: pulp after irradiation reaction 2). The ratio of C1 to C2 can be determined at will in response to pulp quality goals.

[0046] The irradiation reactor basically consists of an irradiation source section and a pulp slurry container section, and the present invention is not specifically limited to either the internal irradiation type in which the irradiation source section exists inside the pulp slurry container section or the external irradiation type in which the irradiation source section exists outside the pulp slurry container section [see Sugimori Akira: "Photochemistry, Chapter 8 Experimental methods of photochemistry I" (Shokabo Publishing Co., Ltd. 1998) pp. 126 - 136]. It is necessary to provide a barrier against gases such as air normally existing around the light source section from which light is emitted to a pulp slurry. In this regard, the choice of the barrier material is important in order that light energy may permeate through the barrier without being attenuated.

[0047] In the present invention, a hard glass barrier can be used in combination with light at a wavelength longer than e.g., 300 nm, while a quartz glass barrier is used in combination with light at a wavelength shorter than 254 nm. The materials of parts of the pulp slurry container not involved in light transmission reaction can be selected from suitable materials less sensitive to the light wavelength used.

**[0048]** An example of an irradiation reactor is shown in Figure 2. An acid-treated pulp is conditioned to a temperature, pH and pulp consistency suitable for irradiation reaction and optionally combined with additives such as reducing agents if desired, and then injected as slurry (a1) into a reaction chamber (20) via (25). The injected pulp slurry undergoes irradiation reaction with light generated from an irradiation source (22) and having passed through the barrier (21: quartz glass tube) while it flows within the reactor (20), after which it is discharged from an outlet (26) of the reactor.

**[0049]** If desired, a gas can be supplied via a diffuser (24) fitted to the irradiation reactor (20). This allows the pulp consistency in the irradiation reactor (20) to be controlled (in terms of % by volume because of the low gas density), whereby the retention time of the pulp in the irradiation reactor (20) or the irradiation reaction period can be controlled at will. The type of the gas used here is preferably air or an inert gas such as nitrogen, and such gas is used as fine bubbles dispersed in a pulp slurry.

**[0050]** When a gas such as hydrogen, oxygen or ozone is used among photoreaction promoters, it can also be supplied via this diffuser (24).

**[0051]** When light at a wavelength range of 135 - 242 nm is used as an irradiation source and air or oxygen is injected as a light source cooling gas (b1) as shown in Figure 2, ozone exists in the gas discharged from the irradiation section.

This discharged gas containing ozone can be injected into a pulp slurry in the irradiation reactor (20) via diffuser (24), whereby the ozone can be used as a reaction promoter without supplying ozone from any external source. The generated ozone can be used not only as an irradiation reaction promoter but also for normal ozone bleaching. It can also be used in combination with a gas effective as an irradiation reaction promoter such as hydrogen, oxygen or ozone injected from an external source. The use of these gases can be selected at will by providing a three-way valve (23a, 23b).

**[0052]** The irradiation reactor can be fitted at will with accessory equipments such as temperature/pH controller, gas concentration detector, etc., if desired.

[0053] The irradiation treatment of the present invention can be repeated one or more times in any manner that can be selected as appropriate depending on a situation such as bleaching efficiency, pulp quality goals (brightness), or the relationship with other bleaching processes used in combination. Examples of manners of repeating the irradiation treatment one or more times are as follows. (1) Two or more irradiators shown in Figure 1 can be provided. In this case, they can be arranged in a series or in parallel. (2) Multiple irradiation sources (which may have identical or different characteristics) can be placed in the irradiator shown in Figure 1. (3) Pulp can be recycled in the system shown in Figure 1. [0054] The bleaching process of the present invention can be combined with any other known chlorine or chlorine-free bleaching process. Specifically, another bleaching process can be followed by the bleaching process of the present invention, or the bleaching process of the present invention can be followed by another bleaching process. Especially, bleaching of the present invention is preferably followed by a hydrogen peroxide treatment. These sequences can be repeated multiple times, and a washing stage can be inserted between different bleaching processes. The bleaching sequence incorporating an irradiation system can also be repeated multiple times. When the irradiation treatment is performed multiple times, the irradiation treatment is preferably followed by washing.

[0055] Embodiments of the second invention are explained below.

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The present invention relates to a high brightness chemical pulp having an ISO brightness of 88% or more and a brightness loss of 1.0% or less in the fading test described below. That is, our studies revealed that the discoloration of paper evaluated by the fading test using UV light as described below shows a good correlation with the actual discoloration, rather than the conventional thermal fading test.

[0056] A hand-made paper is prepared according to JIS P 8222 and irradiated with a xenon lamp at an intensity of 67 W/m² for 30 minutes in an atmosphere at 30°C according to fading test method B of J. TAPPI No.21 Paper and Paperboard (using a xenon arc lamp light fastness tester) and then the ISO brightness is measured and a loss from the ISO brightness before treatment is determined. The chemical pulp used in the present invention can be obtained by using known cooking processes such as kraft cooking, polysulfide cooking, sodium hydroxide cooking or alkaline sulfite cooking, among which kraft cooking is preferred in terms of pulp quality and energy efficiency. Kraft cooking processes include known modified cooking processes such as MCC, EMCC, ITC, and Lo-solids processes, any of which can be applied to the present invention without limitation. Wood can be kraft-cooked under known conditions, for e.g., under conditions described below. The sulfidity of the cooking liquor is 7 - 75%, preferably 15 - 45%, the effective alkali content is 5 - 30% by weight, preferably 10 - 25% by weight on the basis of the bone dry weight of wood, and the cooking temperature is 140 - 170°C. The cooking process may be in a continuous mode or a batch mode, and the type of cooker is not specifically limited.

[0057] The chemical pulp used in the present invention is obtained by washing an unbleached chemical pulp obtained by a known cooking process, passing it through coarse screening and fine screening steps and then subjecting it to an oxygen delignification treatment. The oxygen delignification can be performed under known conditions. In the case of hardwood chemical pulps, the kappa number after oxygen delignification is typically in the range of 5 - 15, preferably 7 - 15, more preferably 8 - 12. This oxygen delignification treatment is performed by a known, medium consistency process or high consistency process. For example, typical reaction conditions for the medium consistency process include a pulp consistency of 10 - 18% by weight, a temperature of 100 - 110°C, a reaction period of 60 - 120 minutes, and a pressure in the reactor of 3 - 6 kg/m², and the sodium hydroxide content and the oxygen content are adjusted depending on the target kappa number.

[0058] In the preparation of the high brightness chemical pulp of the present invention, it is preferable to use a pulp having undergone oxygen delignification followed by an acid treatment. The type of the acid used in the acid treatment of the pulp may be inorganic or organic. Inorganic acids that can be used include mineral acids such as sulfuric acid, hydrochloric acid, nitric acid, sulfurous acid, nitrous acid, phosphoric acid, and residual acids in chlorine dioxide generators. Sulfuric acid is preferred. Organic acids that can be used include acetic acid, lactic acid, oxalic acid, citric acid, formic acid, etc. Hardwood pulps are desirably acid-treated in a pH range of 1.5 - 6.0, preferably 1.0 - 5.0, more preferably 2.0 - 5.0, most preferably 2.5 - 3.5. If the pH is less than 1.0, hexenuronic acid and metal ions are sufficiently removed, but the pulp viscosity greatly decreases because of excessive acidity. If the pH exceeds 6.0, however, the acid concentration is so low that hexenuronic acid and metal ions are insufficiently removed. Hardwood chemical pulps can be acid-treated at lower temperatures in a pH range of 2.5 - 3.5, which leads to the advantage that the acid treatment cost can be reduced.

[0059] The acid treatment can be performed at an atmospheric pressure or under pressure. For example, the reaction

temperature during the acid treatment at an atmospheric pressure is in the range of 80°C or higher and lower than 100°C. Preferably, it is 80 - 95°C, more preferably 80 - 90°C. Temperatures of 30°C or higher and lower than 80°C are effective for removing metals but not effective for removing hexenuronic acid.

[0060] After the acid treatment, the pulp is continuously bleached by a multistage bleaching process. Chemicals used include those consisting of known bleaching agents such as atomic chlorine (C), sodium hydroxide (E), hypochlorites (H), chlorine dioxide (D), oxygen (O), hydrogen peroxide (P), ozone (Z), sulfuric acid (A), and organic peracids in combination with bleaching additives, and any combination appropriately selected from the above list is used as bleaching chemicals. The bleaching sequence is not specifically limited, and examples that can be used include sequences including atomic chlorine and chlorine bleaching chemicals such as C/D-E/O-H-D; ECF bleaching sequences free from atomic chlorine such as D-E-D, Z-E/O-D; and TCF bleaching sequences totally free from chlorine chemicals such as Z-E-P, A-Z-E/O-P.

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**[0061]** The high brightness chemical pulp of the present invention is preferably prepared by a process further comprising irradiating the bleached chemical pulp obtained by the process described above with UV light and/or visible light. The bleached chemical pulp before light treatment preferably has been bleached to an ISO brightness of 80% or more, preferably. 86% or more. For example, very high brightness pulp can be easily obtained by introducing a peroxide bleaching stage after the light treatment stage.

**[0062]** The irradiation treatment with UV light and/or visible light is preferably performed under alkaline conditions. The alkaline conditions are preferably in a pH range of 10 - 13. The alkalis that can be used for this pH adjustment include normal alkaline chemicals, among which sodium hydroxide is preferred. The acids that can be used for the pH adjustment include normal acidic chemicals, among which sulfuric acid is preferred.

**[0063]** The pulp consistency during the irradiation treatment with UV light and/or visible light is preferably 0.1 - 12% by weight. Consistencies lower than 0.1% by weight are not preferred because energy efficiency decreases though bleaching reaction efficiency increases. Consistencies higher than 12% by weight are not preferred because the rheology of pulp slurry in the bleacher decreases so that bleaching reaction efficiency decreases.

**[0064]** The temperature during the irradiation treatment with UV light and/or visible light is not specifically limited, either, but preferably 20 - 95°C. Temperatures lower than 20°C are not preferred because bleaching reaction efficiency is low while temperatures exceeding 95°C are not preferred, either, because pulp quality may deteriorate or the pressure in the reactor may exceed atmospheric pressure so that the reactor must be designed to resist pressure.

**[0065]** The irradiation period of UV light and/or visible light can be determined as appropriate by taking into account the structures or concentrations of potential coloring matters contained in the material pulp.

[0066] The UV light and/or visible light used in the present invention is not specifically limited, but it is desirable to use UV light and/or visible light at a wavelength of about 100 - 400 nm, preferably 200 - 360 nm. UV light at a wavelength shorter than 100 nm is not preferred because photodegradation of cellulose is promoted so that pulp strength and brightness are greatly lowered, while UV light at a wavelength exceeding 400 nm is not preferred, either, because coloring matters are insufficiently photoexcited so that light bleaching performance is greatly lowered.

[0067] Irradiation sources that can be used include conventional light sources such as low-pressure mercury lamps, highpressure mercury lamps, and xenon lamps as well as various excimer lamps and various lasers, but when a large amount of pulp is to be treated, it is desirable to use a high power ozone-generating low-pressure mercury lamp. Ozone-generating UV lamps mainly emit UV light at a wavelength of 254 nm and also include UV light at a wavelength of 185 nm and visible light. The irradiation intensity of UV light at a wavelength of 185 nm is not influenced by temperature, but the intensity of UV light at a wavelength of 254 nm is temperature-dependent and reaches its maximum at 20 - 40°C. Thus, high power ozone-generating lamps having a high surface temperature are cooled with air, and at the same time, ozone gas is generated from oxygen in the air by UV light at a wavelength of 185 nm. In the case of wastewater treatment, this ozone gas decomposes by UV light at a wavelength of 254 nm to produce a highly active oxygen species which remarkably promotes decomposition of coloring components. In contrast to wastewater treatment in which the treatment efficiency improves as the ozone concentration increases, excessive ozone not only blocks UV light at a wavelength of 254 nm, which is the most effective UV light for pulp bleaching, to invite bleaching efficiency loss but also accelerates damage to cellulose fibers by a lot of active oxygen species generated from high concentration ozone to invite significant paper strength loss. Thus, an optimum amount of ozone should be supplied, and such an amount is controlled as appropriate depending on the structures or amounts of coloring matters in the pulp.

**[0068]** In the present invention, all of the known reducing agents, oxidizing agents and hydrogen-donating organic compounds can be used as light bleaching promoters. Such reducing agents include, for example, hydrosulfite and borohydride compounds, etc.; oxidizing agents include hydrogen peroxide; sodium percarbonate, peracetic acid, etc.; and hydrogen-donating organic compounds include primary alcohols such as ethanol. Additives in the present invention may be used alone without using solvents, but should desirably be used as dispersions or solutions in solvents transparent to UV/visible light. Different additives can also be used as mixtures. Such solvents include water, alcohols, linear or cyclic alkanes, ethers, etc. as single solvents or mixed solvents thereof, preferably water. The amount of each additive to be used is not specifically limited so far as it is at or below the saturated concentration of the additive in the solvent,

but a suitable amount is preferably 0.01 - 40% by weight, more preferably 0.1 - 20% by weight in the solvent.

**[0069]** Although the reason why the high brightness chemical pulp obtained by the present invention shows very little discoloration is not clear, it is assumed that discoloration is not induced by relatively weak UV light emitted from the lamp used in the fading test because materials responsible for coloration involved in discoloration remaining in the pulp have been preliminarily decomposed by a very intense UV light at 254 nm and removed.

**[0070]** Papers containing the high brightness chemical pulp of the present invention can be used as not only book papers but also offset printing papers, relief printing papers, gravure printing papers, newsprint papers, electrophotographic papers, or base papers for coated papers, inkjet recording papers, thermosensitive recording papers, pressure sensitive recording papers or the like.

**[0071]** In addition to the high brightness chemical pulp of the present invention, papers containing the high brightness chemical pulp of the present invention may use other raw pulps such as chemical pulps, mechanical pulps and deinked pulps alone or in admixture at any ratio. The pH during the papermaking process may be acidic or neutral or alkaline.

**[0072]** Papers containing the high brightness pulp of the present invention can contain paper strength enhancers. Examples of paper strength enhancers include starches, modified starches, polyacrylamide, polyvinyl alcohol, polyamide-polyamine resins, urea-formalin resins, melamine-formalin resins, polyethylene imines, etc. The paper strength enhancers are preferably contained in an amount of 0.1% by weight or more and 2% by weight or less on the basis of the bone dry weight of the pulp.

**[0073]** Papers containing the high brightness pulp of the present invention can contain fillers. Fillers that can be used include known fillers such as white carbon, talc, kaolin, clay, ground calcium carbonate, precipitated calcium carbonate, titanium oxide, synthetic resin fillers, etc.

**[0074]** Papers containing the high brightness pulp of the present invention can further contain aluminum sulfate, sizing agents, yield improvers, freeness improvers, colorants, dyes, antifoaming agents, bulking agents, fluorescent whitening agents or the like, if desired.

[0075] Papers containing the high brightness pulp of the present invention may not be coated or may be coated with a pigment-free finishing agent. Non-coated papers are desirably coated with a finishing agent based on a water-soluble polymer for the purpose of improving surface strength or sizing performance. Suitable water-soluble polymers include commonly used finishing agents such as starches, modified starches, polyacrylamide, polyvinyl alcohol, etc. alone or as mixtures thereof. In addition to the water-soluble polymers, the finishing agents can also contain paper strength enhancers designed to improve water resistance or surface strength and external sizing additives designed to provide sizing performance. The finishing agents can be applied with coaters such as two-roll size press coaters, gate roll coaters, blade metering coaters, rod metering coaters, etc. The finishing agents are preferably applied in an amount of 0.1 g/m<sup>2</sup> or more and 3 g/m<sup>2</sup> or less per side.

#### **EXAMPLES**

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**[0076]** The following examples further illustrate the present invention in detail without, however, limiting the invention thereto.

<Determination of physical properties of pulp>

Determination of kappa number: performed according to JIS P 8211.

**[0077]** Determination of pulp brightness: Pulp was defibrated and then formed into a sheet having a basis weight of 60 g/m<sup>2</sup> according to Tappi test method T205os-71 (JIS P 8222), and measured for pulp brightness according to JIS P 8148.

<Experimental apparatus>

[0078] The experimental apparatus used in the examples below is shown in Figure 3.

**[0079]** An irradiation reaction chamber (1) consists of a 3L glass cylinder (100 mm f x 620 mm H). This irradiation reaction chamber (1) is equipped with a temperature controller and a pH meter in addition to a stirrer (4) and a diffuser tube (5) shown in the figure. An irradiation source (16W low-pressure mercury lamp, AY-1 from Photoscience Japan Corporation) is placed in a quartz glass tube (45 mm f x 470 mm H, thickness 2 mm) in such a manner that air can be injected around the irradiation source.

[Example 1]

[0080] An oxygen-delignified hardwood kraft pulp available from Nippon Paper Group, Inc. (kappa number 11.6, ISO

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brightness 45.6%) was used.

**[0081]** An acid treatment was performed under the following conditions to give a pulp having a kappa number of 5.5 and a brightness of 47.5%.

**[0082]** Acid treatment conditions: pulp consistency 10% by weight, pH 3.0 (adjusted with sulfuric acid), temperature 95°C, treatment period 180 minutes. After the treatment was completed, the pulp was washed with water.

[0083] A 5 g (bone dry weight) portion of the acid-treated pulp thus obtained was collected and diluted to a pulp consistency of 0.25% by weight and then prepared into pulp slurries at pHs over an acidic to alkaline range using NaOH and  $H_2SO_4$ . These slurries were injected into the experimental apparatus shown in Figure 3, and subjected to an irradiation reaction while stirring under conditions of a temperature of  $25^{\circ}$ C for a treatment period of 120 minutes using a low-pressure UV lamp having a dominant wavelength at 254 nm. After the reaction was completed, the pulps were washed and then formed into sheets and measured for brightness. The results are shown in Figure 4 and Table 1.

#### [Example 2]

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15 **[0084]** The same oxygen-delignified hardwood kraft pulp as used in Example 1 was treated with ozone under the following conditions to give a pulp having a kappa number of 3.0 and a brightness of 56.6%.

**[0085]** Ozone treatment conditions: pulp consistency 10%, ozone feed 7 kg/ADTP, temperature 50°C, treatment period 30 seconds, pH 2.5 (adjusted with sulfuric acid).

**[0086]** A 5 g (bone dry weight) portion of the ozone-treated pulp thus obtained-was collected and prepared into pulp slurries at pHs over an acidic to alkaline range and subjected to an irradiation reaction under similar conditions to those of Example 1, and the resulting pulps were measured for brightness. The results are shown in Figure 4 and Table 1.

#### [Comparative example 1]

[0087] A 5 g (bone dry weight) portion of the same oxygen-delignified hardwood kraft pulp as used in Example 1 was collected and prepared into pulp slurries at pHs over an acidic to alkaline range and subjected to an irradiation reaction under similar conditions to those of Example 1, and the resulting pulps were measured for brightness. The results are shown in Figure 4 and Table 1.

# 30 [Table 1]

#### [8800]

Table 1

35  PH Example 1 Example 2 Comparative example 1  2.84 60.24 67.84  4.69 57.95 71.41  7.77 58.75 69.26  9.48 60.3 74.67 55.58  10.43 66.15 77.41 58.83	_				
2.84 60.24 67.84 4.69 57.95 71.41 7.77 58.75 69.26 9.48 60.3 74.67 55.58	35			ISO bright	ness (%)
4.69 57.95 71.41 7.77 58.75 69.26 9.48 60.3 74.67 55.58		рН	Example 1	Example 2	Comparative example 1
7.77 58.75 69.26 9.48 60.3 74.67 55.58		2.84	60.24	67.84	
9.48 60.3 74.67 55.58	40	4.69	57.95	71.41	
		7.77	58.75	69.26	
10.43 66.15 77.41 58.83		9.48	60.3	74.67	55.58
		10.43	66.15	77.41	58.83
45         11.75         71.19         82.36         61.85	45	11.75	71.19	82.36	61.85
12.61 67.7 77.83 62.9		12.61	67.7	77.83	62.9

# [Example 3]

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**[0089]** A 5 g (bone dry weight) portion of the same acid-treated pulp as used in Example 1 was collected and diluted to a pulp consistency of 0.25% by weight and then prepared into a pulp slurry at pH 11.5 (adjusted with NaOH and  $H_2SO_4$ ). This slurry was injected into the experimental apparatus shown in Figure 3, and subjected to an irradiation reaction while stirring under conditions of a temperature of 25°C for varying treatment periods using a low-pressure UV lamp having a dominant wavelength at 254 nm. After the reaction was completed, the pulps were washed and then formed into sheets and measured for brightness. The results are shown in Figure 5 and Table 2.

#### [Example 4]

**[0090]** A 5 g (bone dry weight) portion of the same ozone-treated pulp as used in Example 2 was collected and subjected to an irradiation reaction under similar conditions to those of Example 3 for varying treatment periods and measured for brightness. The results are shown in Figure 5 and Table 2.

#### [Comparative example 2]

**[0091]** A 5 g (bone dry weight) portion of the same oxygen-delignified hardwood kraft pulp as used in Comparative example 1 was collected and subjected to an irradiation reaction under similar conditions to those of Example 3 for varying treatment periods and measured for brightness. The results are shown in Figure 5 and Table 2.

Table 2

#### *15* [0092]

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[Table 2]

	ISO brightness (%)				
UV irradiation period (h)	Example 3	Example 4	Comparative example 2		
0	47.5	56.57	47.5		
0.5	55.57	70.97			
1	62.87	79.05			
2	71.19	82.36	61.85		
4	78.59	85.5	66.75		
8	85.69	85.86	79.59		

[Example 5]

**[0093]** An oxygen-delignified softwood kraft pulp available from Nippon Paper Group, Inc. (kappa number 9.1, ISO brightness 33.3%) was used.

**[0094]** An acid treatment was performed under the following conditions to give a pulp having a kappa number of 9.1 and a brightness of 34.3%.

**[0095]** Acid treatment conditions: pulp consistency 10% by weight, pH 3.0 (adjusted with sulfuric acid), temperature 95°C, treatment period 180 minutes. After the treatment was completed, the pulp was washed with water.

[0096] A 5 g (bone dry weight) portion of the acid-treated pulp thus obtained was collected and diluted to a pulp consistency of 0.25% by weight and then prepared into pulp slurries at pHs over an acidic to alkaline range using NaOH and  $H_2SO_4$ . These slurries were injected into the experimental apparatus shown in Figure 3, and subjected to an irradiation reaction while stirring under conditions of a temperature of  $25^{\circ}$ C for a treatment period of 120 minutes using a low-pressure UV lamp having a dominant wavelength at 254 nm. After the reaction was completed, the pulps were washed and then formed into sheets and measured for brightness. The results are shown in Figure 5 and Table 3.

[Comparative example 3]

**[0097]** A 5 g (bone dry weight) portion of the same oxygen-delignified softwood kraft pulp as used in Example 5 was collected and prepared into pulp slurries at pHs over an acidic to alkaline range and subjected to an irradiation reaction under similar conditions to those of Example 5, and the resulting pulps were measured for brightness. The results are shown in Figure 6 and Table 3.

Table 3

*55* **[0098]** 

#### [Table 3]

	ISO brightness (%)				
рН	Example 5 Comparative example				
10.43	44.52	41.1			
11.75	54.89	48.02			
12.61	57.24	47.56			
13.1	54.31	48.23			

#### [Example 6]

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[0099] An oxygen-delignified hardwood kraft pulp available from Nippon Paper Group, Inc. (kappa number 9.5, ISO brightness 47.5%) was used.

**[0100]** An acid treatment was performed under the following conditions to give a pulp having a kappa number of 5.5 and a brightness of 48.6%.

**[0101]** Acid treatment conditions: pulp consistency 10% by weight, pH 3 (adjusted with sulfuric acid), temperature 85°C, treatment period 180 minutes. After the treatment was completed, the pulp was washed with water.

**[0102]** A 5 g (bone dry weight) portion of the acid-treated pulp thus obtained was collected and diluted to a pulp consistency of 0.5% by weight and then prepared into a pulp slurry at pH 11.5 with NaOH. This slurry was injected into the experimental apparatus shown in Figure 3, and subjected to an irradiation reaction while stirring under conditions of a temperature of 25°C for a treatment period of 120 minutes using a low-pressure UV lamp having a dominant wavelength at 254 nm. After the reaction was completed, the pulp was washed and then formed into a sheet and measured for brightness. The results are shown in Table 4.

#### [Comparative example 4]

**[0103]** A 15 g (bone dry weight) portion of the same acid-treated pulp as used in Example 6 was collected and diluted to a pulp consistency of 0.5% by weight and then injected into the experimental apparatus shown in Figure 3, and subjected to an ozone treatment while stirring at a temperature of 25°C, pH 11.5 for 120 minutes (without using an irradiation source). The accumulated ozone feed to the pulp during the time was 0.7% by weight. The results are shown in Table 4.

# 35 [Example 7]

**[0104]** A 15 g (bone dry weight) portion of the same acid-treated pulp as used in Example 6 was collected and diluted to a pulp consistency of 0.5% by weight and then injected into the experimental apparatus shown in Figure 3, and subjected simultaneously to an ozone treatment and an irradiation reaction while stirring at a temperature of 25°C, pH 11.5 for 120 minutes using a low-pressure UV lamp having a dominant wavelength at 254 nm. The accumulated ozone feed to the pulp during the time was 0.7% by weight. The results are shown in Table 4.

### [Example 8]

[0105] The same oxygen-delignified hardwood kraft pulp as used in Example 1 (kappa number 11.6, ISO brightness 45.6%) was treated with ozone under the following conditions to give a pulp having a kappa number of 3.0 and a brightness of 56.6%.

 $\textbf{[0106]} \quad \text{Ozone treatment conditions: pulp consistency 10\%, ozone feed 7 kg/ADTP, temperature 55°C, treatment period 30 seconds, pH 2.5.}$ 

[0107] A 15g (bone dry weight) portion of the ozone-treated pulp thus obtained was collected and diluted to a pulp consistency of 0.5% by weight and then injected into the experimental apparatus shown in Figure 3, and subjected to an irradiation reaction while stirring at a temperature of 25°C, pH 11.5 for 120 minutes using a low-pressure UV lamp having a dominant wavelength at 254 nm. The results are shown in Table 4.

[0108]

[Table 4]

	Pulp	Treatment method	ISO brightness after treatment	Gain after treatment
Example 6	After acid treatment with heating	Irradiation treatment alone	60.4%	11.8%
Comparative example 4	After acid treatment with heating	Ozone treatment alone	51.7%	3.1%
Example 7	After acid treatment with heating	Combination of ozone treatment and irradiation treatment	72.2%	23.6%
Example 8	After ozone treatment	Irradiation treatment	74.7%	18.1%

<Evaluation of physical properties of pulp>

#### [0109]

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- 5 Determination of kappa number: performed according to JIS P 8211.
  - Determination of pulp brightness: Pulp was defibrated and then formed into a sheet having a basis weight of 60 g/m<sup>2</sup> according to JIS P 8222, and measured for pulp brightness according to JIS P 8148.

<Experimental apparatus>

**[0110]** The experimental apparatus used in the examples below is shown in Figure 3. An irradiation reaction chamber (20) consists of a 4L glass cylinder (100 mm f x 620 mm H). This irradiation reaction chamber (20) is equipped with a temperature controller and a pH meter in addition to a stirrer (27) and a diffuser tube (24) shown in the figure. An irradiation source (16W low-pressure mercury lamp, AY-1 from Photoscience Japan Corporation) is placed in a quartz glass tube (25 mm f x 470 mm H, thickness 2 mm) in such a manner that air can be injected around the irradiation source. In the examples below, two such irradiation sources were used.

[Example 9]

- 20 [0111] An oxygen-delignified hardwood kraft pulp available from Nippon Paper Group, Inc. (kappa number 11.6, ISO brightness 45.6%) was acid-treated at a pulp consistency of 10% by weight, pH 3.0 (adjusted with sulfuric acid), at a temperature of 95°C for a treatment period of 180 minutes. After the acid treatment was completed, the pulp was washed with water to give a pulp having a kappa number of 5.5 and a brightness of 47.5%.
  - **[0112]** A 15 g (bone dry weight) portion of the acid-treated pulp was collected and prepared into a pulp slurry having a consistency of 0.5% by weight with water, and then the pulp slurry was adjusted to pH 11.5 with NaOH. This pulp slurry was injected into the experimental apparatus shown in Figure 3, and subjected to an irradiation reaction while stirring under conditions of a temperature of 25°C for a treatment period of 120 minutes using a low-pressure UV lamp having a dominant wavelength at 254 nm. Simultaneously, the air injected into the quartz glass tube shown in Figure 3 to cool the light source was discharged via the diffuser and ozone was fed. After the treatment was completed, the pulp was washed and then formed into a sheet and measured for brightness. The results are summarized in Table 5.

[Example 10]

**[0113]** Irradiation treatment and ozone feeding were performed under similar conditions to those of Example 9 except that the pulp slurry was adjusted to pH 2.9 with sulfuric acid, after which the resulting pulp was measured for brightness. The results are summarized in Table 5.

[Example 11]

40 [0114] Irradiation treatment and ozone feeding were performed under similar conditions to those of Example 1 except that the pulp slurry was treated at pH 6.6 without pH adjustment, after which the resulting pulp was measured for brightness. The results are summarized in Table 5.

[Comparative example 5]

**[0115]** Irradiation treatment was performed under similar conditions to those of Example 9 except that ozone feeding was omitted (i.e., air was not injected into the quartz glass tube shown in Figure 3 but directly introduced into the diffuser to feed the pulp slurry), after which the resulting pulp was measured for brightness. The results are summarized in Table 5.

[Comparative example 6]

**[0116]** Reaction was performed under similar conditions to those of Example 9 except that irradiation treatment was omitted (i.e., the light source was not turned on) and the ozone (concentration 50 ppm) generated from an ozone generator (ozone spray, NS-3 available from Kankyo Kogaku Co., Ltd.) was fed via the diffuser shown in Figure 3, after which the resulting pulp was measured for brightness. The results are summarized in Table 5.

[0117]

#### [Table 5]

	Irradiation	Ozone feeding	рН	Brightness (%)
Example 9	Yes	Yes	11.5	73.8
Example 10	Yes	Yes	2.9	70.9
Example 11	Yes	Yes	6.6	63.3
Comparative example 5	Yes	No	11.5	60.4
Comparative example 6	No	Yes	11.5	53.3

**[0118]** As shown in Table 5, pulps with higher brightness can be prepared in Examples 9 - 11 involving irradiation with UV light or visible light or both in the presence of ozone. However, brightness was somewhat lower in Example 11 wherein irradiation was not performed under acidic conditions of pH 2 - 4 or under alkaline conditions of pH 10 - 13.

<Determination of ISO brightness of pulp>

[0119] Determination of pulp brightness: Pulp was defibrated and then formed into a sheet having a basis weight of 60 g/m<sup>2</sup> according to JIP P 8222, and measured for ISO brightness according to JIS P 8148.

<Pulp>

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**[0120]** An oxygen-delignified hardwood kraft pulp (ISO brightness 45.6%, available from Nippon Paper Group, Inc.) was further subjected to acid treatment - ozone bleaching under the following conditions and the resulting pulp was used in the examples and comparative examples below.

- Acid treatment: The oxygen-delignified hardwood kraft pulp was acid-treated at a pulp consistency of 10% by weight, pH 3.0 (adjusted with sulfuric acid), at a temperature of 95°C for a treatment period of 180 minutes. After the treatment was completed, the pulp was washed with water. At this stage, the ISO brightness of the pulp was 47.5%.
- Ozone bleaching: The acid-treated pulp was bleached with ozone at a pulp consistency of 10%, ozone feed 7 kg/
  (1t of air-dried pulp), at a temperature of 50°C for a treatment period of 30 seconds at pH 2.5 (adjusted with sulfuric
  acid). After the treatment was completed, the pulp was washed with water. At this stage, the ISO brightness of the
  pulp was 59.7%.

[Example 12]

**[0121]** The ozone-bleached pulp was further bleached in a bleaching sequence of hydrogen peroxide bleaching 1 - light bleaching - hydrogen peroxide bleaching 2 under the following conditions.

- Hydrogen peroxide bleaching 1: pulp consistency 10% by weight, pH 11.5 (adjusted with sodium hydroxide), temperature 75°C, treatment period 90 minutes. After the treatment was completed, the pulp was washed with water. At this stage, the ISO brightness of the pulp was 75.0%.
- Light bleaching conditions: A 5 g (bone dry weight) portion of the pulp bleached with hydrogen peroxide was collected and diluted to a pulp consistency of 0.25% by weight and then prepared into a pulp slurry at pH 11.5 with sodium hydroxide. This slurry was injected into a 2L glass cylinder, and subjected to an irradiation reaction while stirring at a temperature of 25°C for a treatment period of 15 minutes using a 16W low-pressure UV lamp having a dominant wavelength at 254 nm (AY-1 from Photoscience Japan Corporation). After the treatment was completed, the pulp was washed with water. At this stage, the ISO brightness of the pulp was 78.5%.
- Hydrogen peroxide bleaching 2: The light bleached pulp was treated under the same conditions as those of hydrogen peroxide bleaching 1 above. The final ISO brightness was 85.0%.

[Example 13]

[0122] Bleaching treatment was performed under the same conditions as those of Example 1 except that the treatment period of light bleaching was 30 minutes. The ISO brightness after light bleaching was 80.0%. The resulting light bleached pulp was treated under the conditions of hydrogen peroxide bleaching 2 above. The final ISO brightness was 86.1%.

#### [Example 14]

[0123] Treatment was performed under the same conditions as those of Example 1 except that the treatment period of hydrogen peroxide bleaching 1 was 45 minutes. The ISO brightness after hydrogen peroxide bleaching 1 was 71.0%. The ISO brightness after light bleaching was 74.5%. The resulting pulp was treated under the same conditions as those of hydrogen peroxide bleaching 2 above. The final ISO brightness was 84.1%.

[Example 15]

- 10 **[0124]** The ozone-bleached pulp was further bleached in a bleaching sequence of light bleaching hydrogen peroxide bleaching. Light bleaching was performed under the same conditions as those of Example 12 except that the treatment period was 60 minutes. The brightness after light bleaching was 75.4%. The resulting pulp was treated under the same conditions as those of hydrogen peroxide bleaching 2 of Example 12. The final ISO brightness was 84.3%.
- 15 [Example 16]

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**[0125]** Treatment was performed under the same conditions as those of Example 4 except that the treatment period of light bleaching was 120 minutes. The ISO brightness after light bleaching was 81.8%. The resulting pulp was treated under the same conditions as those of hydrogen peroxide bleaching 2 of Example 12. The final ISO brightness was 85.2%.

[Example 17]

**[0126]** Treatment was performed under the same conditions as those of Example 12 except that the treatment period of hydrogen peroxide bleaching 1 was 30 minutes. The ISO brightness after hydrogen peroxide bleaching 1 was 68.2%. The ISO brightness after light bleaching was 72.3%. The resulting pulp was treated under the same conditions as those of hydrogen peroxide bleaching 2 of Example 12. The final ISO brightness was 81.7%.

[Comparative example 7]

[0127] The ozone-bleached pulp was further bleached in a bleaching sequence of hydrogen peroxide bleaching 1 - hydrogen peroxide bleaching 2. Bleaching treatment was performed under the same conditions as those of Example 12 except that light bleaching was omitted. The final ISO brightness was 79.3%.

[Comparative example 8]

**[0128]** The ozone-bleached pulp was further bleached in a bleaching sequence of hydrogen peroxide bleaching 1 - light bleaching. Light bleaching was performed under the same conditions as those of Example 12 except that the treatment period was 60 minutes. Hydrogen peroxide bleaching 1 was performed under the same conditions as those of Example 12. The final ISO brightness was 83.3%.

[Comparative example 9]

**[0129]** The ozone-bleached pulp was further bleached in a bleaching sequence of hydrogen peroxide bleaching 1 - light bleaching - hydrogen peroxide bleaching 2. Bleaching treatment was performed under the same conditions as those of Example 1 except that light bleaching was performed at pH 4.0 (adjusted with sulfuric acid). The brightness after light bleaching was 75.9%. The resulting pulp was treated under the same conditions as those of hydrogen peroxide bleaching 2 of Example 12. The final ISO brightness was 82.6%.

[0130] The results of Examples 12 - 17 and Comparative examples 7 - 9 are shown in Table 6. [0131]

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[Table 6]

	ISO brightness (%) after hydrogen peroxide bleaching 1	ISO brightness (%) after light bleaching	ISO brightness (%) after hydrogen peroxide bleaching 2
Example 12	75.0	78.5	85.0
Example 13	75.0	80.0	86.1
Example 14	71.0	74.5	84.1
Example 15	-	75.4	84.3
Example 16	-	81.8	85.2
Example 17	68.2	72.3	81.7
Comparative example 7	75.0	-	79.3
Comparative example 8	75.0	83.3	-
Comparative example 9	75.0	75.9	82.6

**[0132]** As shown in Table 6, high brightness pulps were obtained by treating the ozone-bleached pulp in a bleaching sequence of hydrogen peroxide bleaching 1 - light bleaching - hydrogen peroxide bleaching 2. However, the final brightness was somewhat low in Example 6 wherein a pulp having an ISO brightness of less than 70% before the light bleaching treatment. In the sequence of Comparative example 2 wherein hydrogen peroxide bleaching was omitted after light bleaching, the light treatment period had to be greatly extended to obtain an ISO brightness of 80% or more. In Comparative example 9 wherein the pH after light bleaching was acidic, both brightness after light bleaching and final brightness were lower than those of Example 12.

[Example 18]

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[0133] A 200 g (bone dry weight) portion of a bleached hardwood pulp (ISO brightness 85.6%) obtained by the chlorine bleaching process of plant A of Nippon Paper Group, Inc. was collected and diluted to a pulp consistency of 1% and then adjusted to pH 11.5 with sodium hydroxide. This slurry was injected into the experimental apparatus shown in Figure 7, and subjected to a UV light bleaching treatment while stirring at a temperature of 25°C for a treatment period of 120 minutes. When the treatment was completed, the pulp was washed and then formed into a sheet and measured for brightness. The sheet measured for brightness was then used in a fading test. A sheet was prepared from the pulp after defibration and measured for breaking length. The methods for these evaluations are described below, and the results are shown in Table 1.

- Determination of freeness: A pulp slurry having a consistency of 10% was treated at 6000 rev in a PFI mill and then
  measured for freeness (CSF) according to JIS P 8121.
  - Determination of pulp brightness: Pulp was defibrated and then formed into a sheet having a basis weight of 60 g/m<sup>2</sup> according to JIP P 8222, and measured for ISO brightness according to JIS P 8148.
  - Determination of breaking length: Pulp was defibrated and then formed into a sheet having a basis weight of 60 g/m<sup>2</sup> according to JIP P 8222, and measured for breaking length according to JIS P 8113.
  - Fading test: performed with a xenon lamp weatherometer. Samples were irradiated with UV light generated from a xenon lamp for 30 minutes and then measured for ISO brightness (JIS P 8148). The fading test was performed at a temperature of 30°C and an intensity of 67 W/m². In Table 1, Δ brightness and brightness loss are defined as follows:

 $\Delta$  Brightness = ISO brightness after fading test - ISO brightness before fading test.

# Brightness loss = $\Delta$ brightness / ISO brightness before fading test.

- UV light bleaching experimental apparatus: The experimental apparatus used in the example is shown in Figure 7. An ozone-generating low-pressure UV lamp (95 W, 18 mm (f) x 1100 mm (H), SUV110D from Sen Light Corporation) is fixed at the center of a UV light irradiation reaction chamber in the form of a glass cylinder of 72.1 nm (f) x 1180 mm (H) (effective capacity 2.64 L), and the ozone gas generated (540 mg/h) is introduced from the bottom of the reaction chamber and flows upward with pulp slurry in the reaction chamber. After light bleaching, the pulp slurry can be recycled to the reaction chamber by a pump via a stock tank (capacity 30 L).
- 45 [Example 19]
  - [0134] A 200 g (bone dry weight) portion of a bleached hardwood pulp (ISO brightness 84.9%) obtained by the ozone ECF bleaching process [acid treatment (oxygen-delignified pulp consistency 10% by weight, pH 3 (adjusted with sulfuric acid), temperature 85°C, treatment period 180 minutes); ozone treatment (pulp consistency 10% by weight, pH 2.5 (adjusted with sulfuric acid), ozone feed 7 kg/ 1t of air-dried pulp, temperature 55°C, treatment period 30 seconds)] of plant B of Nippon Paper Group, Inc. was collected and diluted to a pulp consistency of 1% and then adjusted to pH 11.5 with sodium hydroxide. This slurry was injected into the experimental apparatus shown in Figure 7, and subjected to a UV light bleaching treatment while stirring at a temperature of 25°C for a treatment period of 120 minutes. When the treatment was completed, the pulp was washed and then formed into a sheet and measured for brightness. The sheet measured for brightness was then used in the fading test. A sheet was prepared from the pulp after defibration and measured for breaking length. The results are shown in Table 7.

[Example 20]

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**[0135]** A 200 g (bone dry weight) portion of a bleached hardwood pulp (ISO brightness 84.3%) obtained by the ECF bleaching process (chlorine dioxide treatment - hydrogen peroxide treatment - chlorine dioxide treatment) of plant C of Nippon Paper Group, Inc. was collected and diluted to a pulp consistency of 1% and then adjusted to pH 11.5 with sodium hydroxide. This slurry was injected into the experimental apparatus shown in Figure 7, and subjected to a UV light bleaching treatment while stirring at a temperature of 25°C for a treatment period of 120 minutes. When the treatment was completed, the pulp was washed and then formed into a sheet and measured for brightness. The sheet measured for brightness was then used in the fading test. A sheet was prepared from the pulp after defibration and measured for breaking length. The results are shown in Table 7.

[Comparative example 10]

**[0136]** A 100 g (bone dry weight) portion of a bleached hardwood pulp (ISO brightness 86%) obtained by the chlorine bleaching process of plant A of Nippon Paper Group, Inc. was collected and diluted to a pulp consistency of 10% and then adjusted to pH 11.5 with sodium hydroxide. This slurry was bleached with 3.0 kg of hydrogen peroxide / 1t of airdried pulp at a temperature of 50°C for a treatment period of 180 minutes. When the treatment was completed, the pulp was washed and then formed into a sheet and measured for brightness. The sheet measured for brightness was then used in the fading test. A sheet was prepared from the pulp after defibration and measured for breaking length. The results are shown in Table 7.

[Comparative example 11]

**[0137]** A bleached hardwood pulp (ISO brightness 89.3%) obtained by a commercially available chlorine dioxide ECF bleaching process was used to form a sheet and measured for brightness. The sheet measured for brightness was then used in the fading test. A sheet was prepared from the pulp after defibration and measured for breaking length. The results are shown in Table 7.

[Comparative example 12]

**[0138]** A bleached hardwood pulp (ISO brightness 85.6%) obtained by the chlorine bleaching process of plant A of Nippon Paper Group, Inc. was used to form a sheet and measured for brightness. The sheet measured for brightness was then used in the fading test. A sheet was prepared from the pulp after defibration and measured for breaking length. The results are shown in Table 7.

[Comparative example 13]

**[0139]** A bleached hardwood pulp (ISO brightness 84.9%) obtained by the chlorine bleaching process of plant B of Nippon Paper Group, Inc. was used to form a sheet and measured for brightness. The sheet measured for brightness was then used in the fading test. A sheet was prepared from the pulp after defibration and measured for breaking length. The results are shown in Table 7.

[0140]

[Table 7]

	ISO brightness (%)		A Prightness (9/)	Prightness loss (9/)	CSF after defibration (mL)	Procking longth (km)
	Before fading test	After fading test	Δ Brightness (%)	Brightness loss (%)	CSF after delibration (IIIL)	Breaking length (km)
Example 18	90.5	90.0	0.5	0.55	370	5.99
Example 19	89.0	88.4	0.6	0.67	372	5.86
Example 20	88.6	88.0	0.6	0.68	376	5.90
Comparative example 10	89.4	86.5	2.9	3.20	375	5.62
Comparative example 11	89.3	86.7	2.6	2.90	365	5.18
Comparative example 12	85.6	82.5	3.1	3.60	385	5.58
Comparative example 13	84.9	82.0	2.9	3.40	380	5.64

#### Claims

- 1. A pulp bleaching process characterized in that a pulp washed after an acid treatment is irradiated with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions.
- 2. The pulp bleaching process of claim 1 characterized in that the alkaline conditions comprise a pH range of 10 13.
- 3. The pulp bleaching process of claim 1 or 2 characterized in that the acid treatment is performed under conditions of pH 1 - 6 and a temperature of 80°C or more.
- 4. The pulp bleaching process of claim 1 or 2 characterized in that the acid treatment is performed in the presence of ozone under conditions of pH 1.0 - 8.0 and a temperature of 25 - 95°C.
- 5. The pulp bleaching process of any one of claims 1 to 4 characterized in that the irradiation treatment is performed 15 in the presence of at least one compound selected from the group consisting of reducing agents, peroxides, and hydrogen-donating organic compounds.
  - 6. The pulp bleaching process of any one of claims 1 to 5 characterized in that the irradiation source of the UV light and/or visible light consists of multiple light sources having different wavelength characteristics.
  - 7. The pulp bleaching process of any one of claims 1 to 6 characterized in that the irradiation treatment is repeated multiple times.
- 8. A pulp bleaching process characterized in that a pulp washed after an acid treatment is irradiated with UV light 25 and/or visible light at a wavelength of 100 - 400 nm in the presence of ozone.
  - 9. The pulp bleaching process of claim 8 characterized in that the irradiation treatment with UV light and/or visible light is performed under acidic conditions of pH 2 - 4 or under alkaline conditions of pH 10 - 13.
- 30 10. The pulp bleaching process of claim 8 or 9 characterized in that the acid treatment is performed under conditions of pH 1 - 6 and a temperature of 80 - 180°C.
  - 11. The pulp bleaching process of any one of claims 8 to 10 characterized in that the acid treatment is performed in the presence of ozone under conditions of pH 1 - 8 and a temperature of temperature 25 - 95°C.
  - 12. The pulp bleaching process of any one of claims 8 to 11 characterized in that the ozone is generated by irradiating air or oxygen or a mixture thereof with UV light.
- 13. The pulp bleaching process of any one of claims 8 to 12 characterized in that the ozone concentration during the 40 irradiation treatment is 0.5 - 100 ppm.
  - 14. A pulp bleacher characterized in that air or oxygen or a mixture thereof is supplied to the surroundings of an irradiation source of UV light and/or visible light to generate ozone and a gas containing the ozone is fed to a pulp.
- 45 15. A pulp bleacher comprising an ozone-generating chamber having an irradiation source for emitting UV light and/or visible light therein and a pulp slurry chamber, wherein the ozone-generating chamber has a gas injection port and a discharge port, and the discharge port communicates with the pulp slurry chamber.
- 16. A totally chlorine-free (TCF) bleaching process for chemical pulp characterized in that an oxygen-delignified pulp 50 is acid-treated and then bleached by a bleaching process used in totally chlorine-free bleaching, and the resulting pulp is further subjected to a light bleaching treatment with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions, followed by alkaline hydrogen peroxide bleaching
  - 17. A totally chlorine-free bleaching process for chemical pulp characterized in that an oxygen-delignified pulp is acidtreated and then bleached by a bleaching process used in normal TCF bleaching to an ISO brightness of 70 - 75%, and the resulting pulp is further subjected to a light bleaching treatment with UV light and/or visible light at a wavelength of 100 - 400 nm under alkaline conditions to an ISO brightness of 75 - 80%, followed by alkaline hydrogen peroxide bleaching to give a pulp having an ISO brightness of 84% or more.

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- **18.** The bleaching process for chemical pulp of claim 1 or 2 **characterized in that** the light bleaching treatment is performed in a pH range of 10 13.
- **19.** The bleaching process for chemical pulp of any one of claims 16 to 18 **characterized in that** the acid treatment is performed under conditions of pH 1 6 and a temperature of 80°C or more.
  - **20.** The bleaching process for chemical pulp of any one of claims 16 to 19 **characterized in that** the light bleaching treatment is performed in the presence of at least one compound selected from the group consisting of oxidizing agents, reducing agents, and peroxides.
  - 21. A high brightness chemical pulp having an ISO brightness of 88% or more and a brightness loss of 1.0% or less in the following fading test: a hand-made paper is prepared according to JIS P 8222 and irradiated with a xenon lamp at an intensity of 67 W/m² for 30 minutes in an atmosphere at 30°C according to fading test method B of J. TAPPI No.21 Paper and Paperboard (using a xenon arc lamp light fastness tester) and then the ISO brightness is measured and a loss from the ISO brightness before treatment is determined.
  - 22. The high brightness chemical pulp of claim 21, which has been treated with UV light and/or visible light and has an ISO brightness of 88% or more.
- 23. A paper containing the high brightness chemical pulp of claim 21 or 22.

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- **24.** A process for preparing a high brightness chemical pulp **characterized in that** a bleached chemical pulp is treated with UV light and/or visible light.
- 25. A process for preparing a high brightness chemical pulp **characterized in that** a bleached chemical pulp having an ISO brightness of 80% or more is treated with UV light and/or visible light to an ISO brightness of 88% or more.

Figure 1

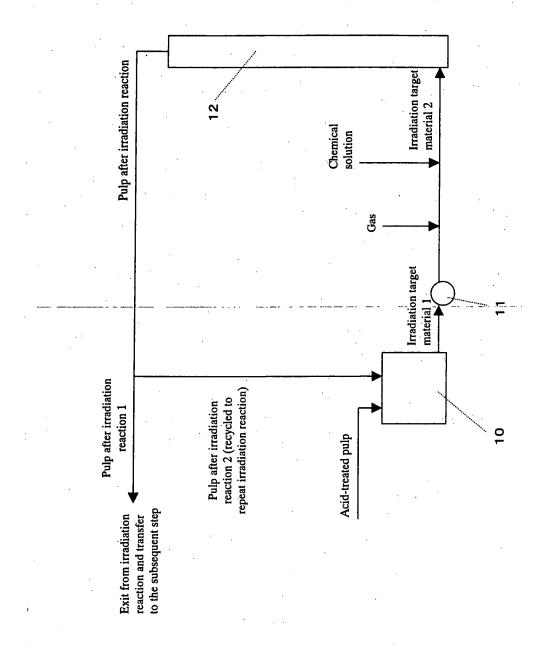
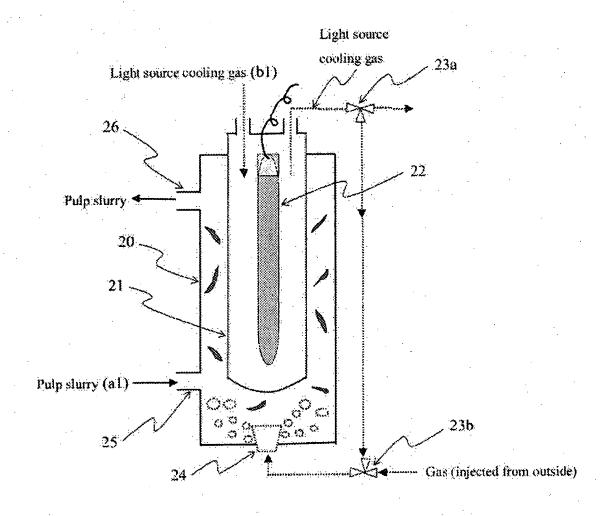
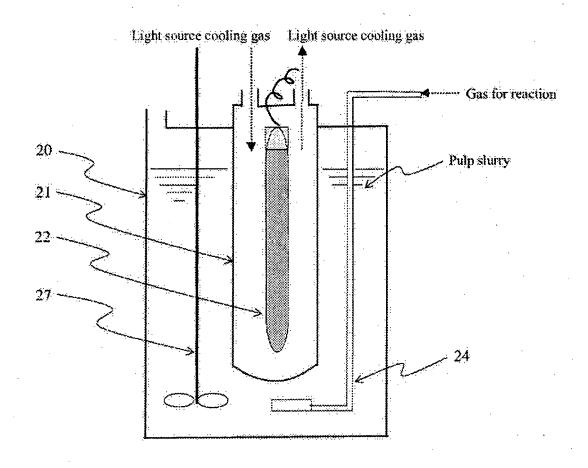


Figure 2



# Figure 3





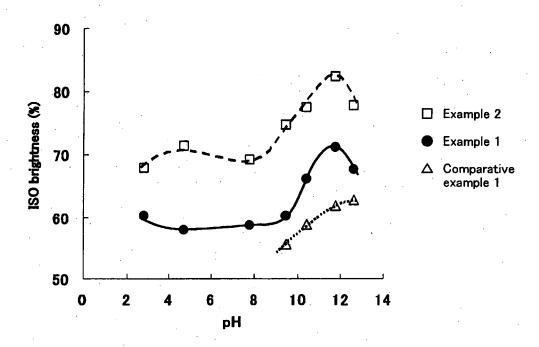
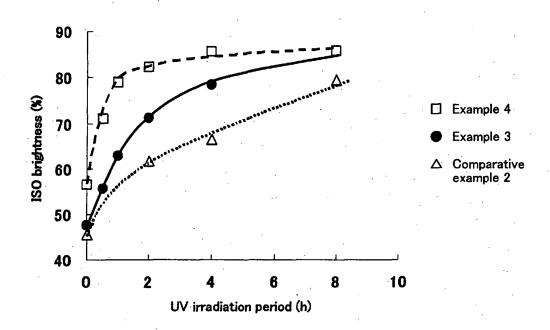


Figure 5





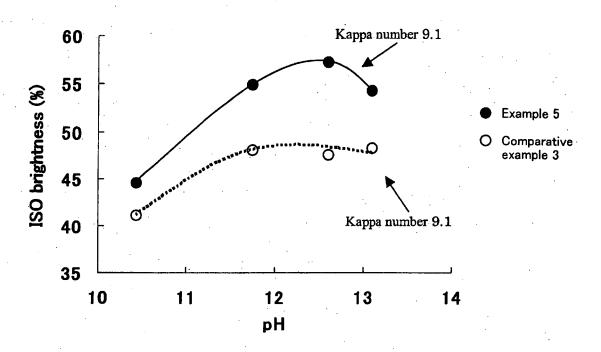
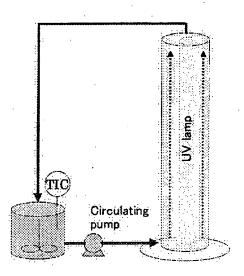


Figure 7



#### INTERNATIONAL SEARCH REPORT International application No. PCT/JP2005/010521 A. CLASSIFICATION OF SUBJECT MATTER Int.Cl<sup>7</sup> D21C9/10 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl<sup>7</sup> D21C9/10 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 1996-2005 Jitsuyo Shinan Toroku Koho Kokai Jitsuyo Shinan Koho 1971-2005 Toroku Jitsuyo Shinan Koho 1994-2005 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DOCUMENTS CONSIDERED TO BE RELEVANT C. Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Χ JP 2002-235293 A (National Institute of 21-23 Advanced Industrial Science and Technology 1-20,24,25 Α (AIST)), 23 August, 2002 (23.08.02), Full text (Family: none) JP 9-241988 A (Mitsubishi Paper Mills Ltd.), Υ 14,15 16 September, 1997 (16.09.97), Full text (Family: none) JP 2003-165711 A (Kabushiki Kaisha Wakomu Υ 14,15 Denso), 10 June, 2003 (10.06.03), Claim 1 (Family: none) X Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive filing date step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be document of particular relevance, the claimed invention varieties considered to involve an inventive step when the document is combined with one or more other such documents, such combination document referring to an oral disclosure, use, exhibition or other means being obvious to a person skilled in the art document published prior to the international filing date but later than "&" document member of the same patent family the priority date claimed Date of the actual completion of the international search Date of mailing of the international search report 29 June, 2005 (29.06.05) 12 July, 2005 (12.07.05) Name and mailing address of the ISA/ Authorized officer Japanese Patent Office

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