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(54) **BLEACHING STAGE USING XYLANASE WITH HYDROGEN PEROXIDE, PERACIDS, OR A COMBINATION THEREOF**

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(57) **ABSTRACT**

The present invention discloses methods of bleaching chemical pulp that combine xylanase enzymes with hydrogen peroxide, peracids, or a mixture. The method comprises the steps of carrying out a chemical pulping operation, optionally followed by delignifying the pulp with oxygen, then combining xylanase enzymes with hydrogen peroxide, peracids, or a mixture to bleach the pulp. The method allows the mill to use both xylanase and peracids in a single bleaching tower to decrease the usage of chlorine dioxide and other bleaching chemicals. The pulp bleaching method of the present invention may be performed in a pulp mill as part of a complex pulp bleaching process.

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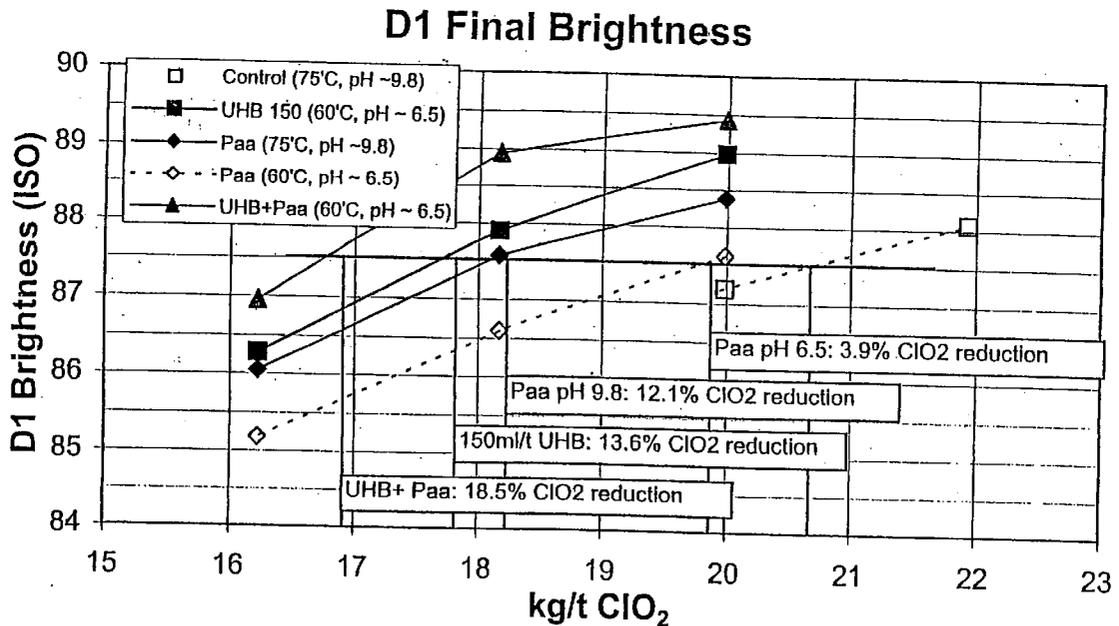


Figure 1. D1 Final Brightness

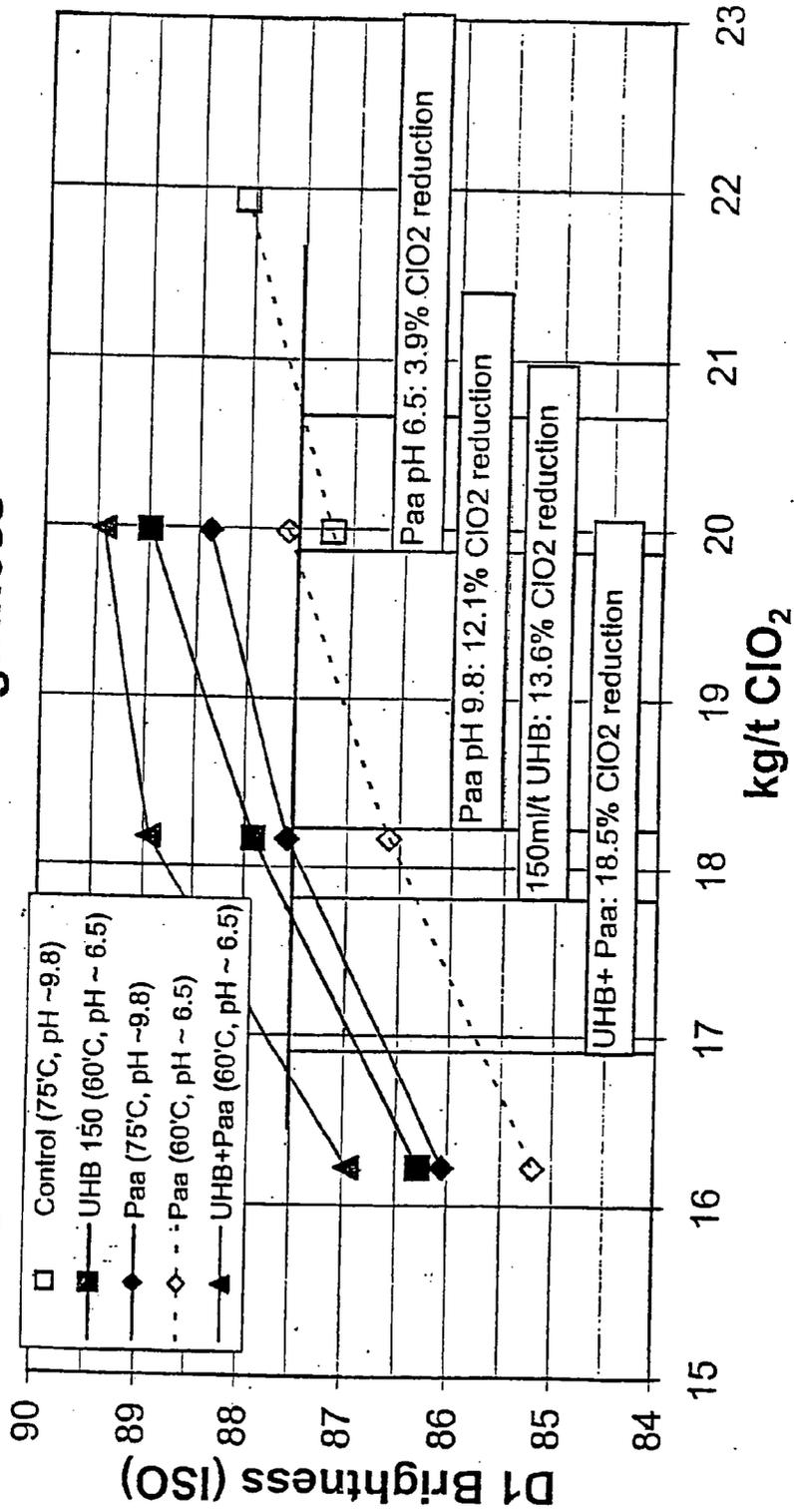
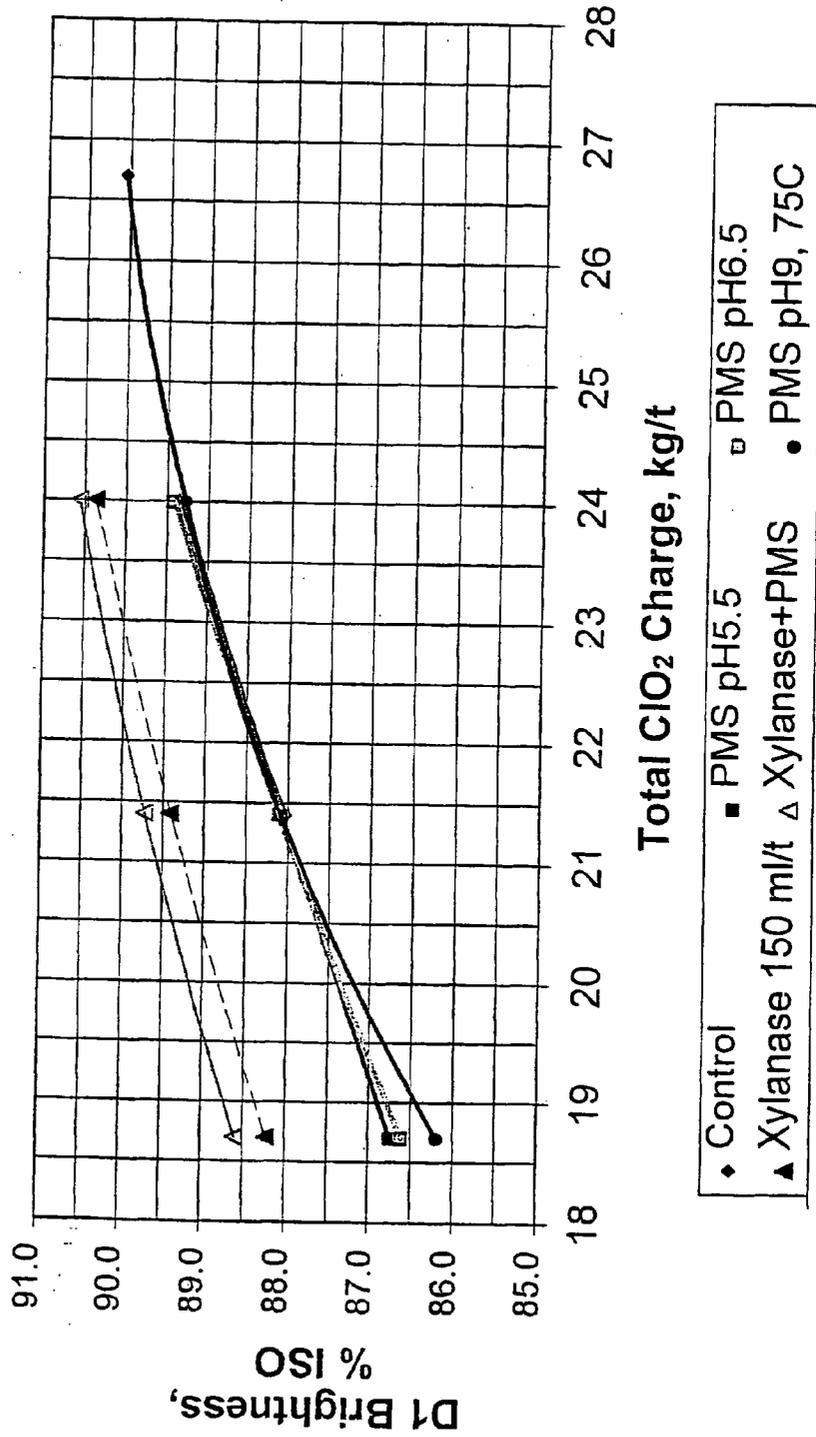


Figure 2. Effect of xylanase and peroxymonosulphate on ClO₂ usage



BLEACHING STAGE USING XYLANASE WITH HYDROGEN PEROXIDE, PERACIDS, OR A COMBINATION THEREOF

[0001] The invention relates to methods of bleaching pulp. More specifically the invention relates to methods of bleaching pulp using xylanase enzymes with hydrogen peroxide, peracids, or a combination thereof.

BACKGROUND OF THE INVENTION

[0002] The production of bleached chemical pulp is a major industry around the world. More than 50 million tons of bleached pulp is produced annually. Bleached chemical pulp is the largest component of all types of white paper, including that used in photocopy paper, writing paper, and paper packaging. In addition, bleached chemical pulp is also used to impart strength to less expensive grades of paper, such as newsprint. Bleached chemical pulp has large markets because of its high degree of whiteness and cleanliness, the stability of the whiteness, its high strength, and the ease and uniformity of the printing surface it provides. These attributes are obtained when lignin, which is colored and decreases the interfiber bonding of the cellulose, is almost completely removed from the pulp.

[0003] In the process of chemical pulping, the furnish (or feedstock) primarily consists of wood chips which are added to a reaction chamber, known as a digester, and are treated with chemicals to dissolve lignin in the pulp. There are several chemical pulping processes known in the art. Two of the major chemical pulping processes are kraft pulping, in which the pulp is cooked in alkaline liquor, and sulfite pulping, in which the pulp is cooked in acidic liquor. Both kraft pulping and sulfite pulping may be performed in batch or continuous digestors.

[0004] One of the main purposes of the pulping process is to release lignin, which binds cellulose fibers in the feedstock. Pulping dissolves 85% to 95% of the lignin in the feedstock material. Following the pulping stage, the pulp is washed with water to remove dissolved lignin.

[0005] While pulping removes most of the lignin in the feedstock material, it is not capable of removing all the lignin without destroying the cellulose fibers of the feedstock. The remaining lignin is removed from the pulp by bleaching.

[0006] A pulp bleaching process may consist of many stages. For example, following pulping, a pulp bleaching process may comprise an alkaline oxygen delignification stage (O), an enzymatic treatment stage (X), one or more chlorine dioxide stages (D), and one or more alkaline extraction stages (E). A pulp bleaching process may also comprise one or more water washes or alternatively, each stage may comprise a water wash as a final step of the stage. Thus, a representative pulp bleaching sequence in which pulp is bleached using three chlorine dioxide stages and two alkaline extraction stages may be represented as D-E-D-E-D. Similarly, a pulp bleaching sequence wherein pulp is subjected to an alkaline oxygen delignification stage, an enzymatic treatment stage, three chlorine dioxide bleaching stages and two alkaline extraction stages wherein each stage is followed by a water wash may be represented by O-X-D-E-D-E-D.

[0007] It is common for mills to perform an alkali-oxygen delignification stage prior to carrying out chemical bleach-

ing of pulp. This process consists of reacting the pulp with oxygen and alkali at high temperatures (approximately 100° C.) for a period of about one hour. Alkali-oxygen delignification reduces the amount of lignin in the pulp by 35-50%, but this process is harsh on the pulp and is often accompanied by destruction of some of the cellulose fibers in the pulp if the extent of delignification is greater than 50%. Following alkali-oxygen delignification, the pulp is washed as described earlier to remove solubilized lignin.

[0008] The next bleaching stage after alkali-oxygen delignification is usually chemical bleaching with oxidative chemicals, the most prominent being chlorine dioxide (ClO₂). However, several processes have been described which may bleach, facilitate bleaching, or enhance bleaching of pulp prior to bleaching with ClO₂. These include (1) the use of hydrogen peroxide and peracids, and (2) the use xylanase enzyme treatment.

[0009] Hydrogen peroxide is a common bleaching chemical. When added to brownstock prior to the bleach plant, it offers the possibility of partially delignifying and/or brightening the pulp (Bleackley, 1991). However, beyond a certain low level of hydrogen peroxide, there is a significant possibility of damaging the fibers.

[0010] The use of xylanase and manganese peroxidase, lignin peroxidase, or laccase enzymes with hydrogen peroxide in combination, or added sequentially, increases the efficiency of hydrogen peroxide (Bermek et al., 2000; Niku-Paavola et al., 1994). Unfortunately, it is not practical to make and use manganese peroxidase lignin peroxidase, or laccase at an industrial scale. However, there is no disclosure in these reports of mixtures comprising hydrogen peroxide and xylanase alone.

[0011] For the past forty years, research has focused on the use of peracids as agents for bleaching pulp. Peracids are formed by reacting hydrogen peroxide with a corresponding acid, i.e. acetic acid with hydrogen peroxide yields peracetic acid. The advantage of converting the hydrogen peroxide to a peracid is that the peracid has a higher oxidation potential, and is therefore a more powerful bleaching agent than the hydrogen peroxide. Peracid in the form of peracetic acid (PAA) is in use as a bleaching chemical in several mills in Scandinavia. Performic acid (the Milox process) has been used in pilot plants, and peroxymonosulfuric acid, peroxonitric acid, and peroxophosphoric acid have been widely studied (Poppius-Levlin et al., 2000).

[0012] The primary processes for making peracids include (1) combining hydrogen peroxide with organic acids such as acetic acid and formic acid to form a percarboxylic acid. The general formula of a percarboxylic acid is R(COO)OOH, where R is an alkyl group (for peracetic acid, R=CH₃). (2) Combining hydrogen peroxide with inorganic acids such as sulfuric acid. The formula of peroxymonosulfuric acid is HO—SO₂—OOH, which is known as Caro's acid. (3) Combining hydrogen peroxide with an activator to form peracids. The activator that has received the most attention is Tetra-acetyl ethylene diamine (TAED).

[0013] Pulp bleaching can be carried out using relatively pure peracids or mixtures of two or more peracids. When used to bleach pulp, the peracids can be produced external to the bleaching stage and added to the pulp, or the reactant chemicals can be added to the pulp and the peracids gener-

ated in situ. One example of the external generation of peracids is the reaction of acetic acid with hydrogen peroxide to form peracetic acid, which is then purified by distillation. A second example of external generation of peracids is the reaction of potassium persulfate with hydrogen phthalate or sulfuric acid to produce peroxymonosulfate (available as Oxone® from Du Pont), which is then added to the pulp (Springer and McSweeney, 1993).

[0014] The in situ generation of peracetic acid has been considered for some time, and involves the addition of hydrogen peroxide and acetic acid, or hydrogen peroxide and acetic anhydride to the pulp. The peracetic acid is generated by the reaction of the peroxide and the acetic acid in the presence of the pulp (Christiansen et al., 1966). As with all bleaching chemicals, the choice of peracid and the process used to generate it depends on the cost of the chemicals and the effectiveness of bleaching.

[0015] Although the interest and mill usage of peracids is increasing, the relatively high cost of the peracids, resulting from the need to combine two or more different chemicals, has limited the use of peracids to this point.

[0016] Xylanase enzymes are used to enhance the bleaching of pulp and to decrease the amount of chlorinated chemicals used in bleaching stages (Erickson, 1990; Paice et al., 1988; Pommier et al., 1989). There have been several mechanisms proposed for the bleaching action of xylanase. One is that lignin is connected to crystalline cellulose through xylan and xylanase enzymes facilitate bleaching of pulp by hydrolysing xylan, releasing coloured lignin from the pulp. A second proposed mechanism is that xylanase removes xylan thereby improving the alkali extractability of the pulp. Regardless of the mechanism, xylanase treatment allows subsequent bleaching chemicals such as chlorine, chlorine dioxide, hydrogen peroxide, or combinations of these chemicals to bleach pulp more efficiently than in the absence of xylanase. Pre-treatment of pulp with xylanase prior to chemical bleaching increases the whiteness and quality of the final paper product and reduces the amount of chlorine-based chemicals that must be used to bleach the pulp. This in turn decreases the chlorinated effluent produced by such processes.

[0017] Xylanases have been isolated from a variety of organisms including bacteria and fungi. Generally, fungal xylanases exhibit optimal activity at acidic pHs, in the range of about 3.5 to 5.5, and a temperature of about 50° C. In contrast, bacterial xylanases exhibit optimal activity at pH 5 to pH 7 and a temperature optimum between 50° C. and 70° C. However, there are other xylanase enzymes that exhibit optimal activity under other conditions. For example, U.S. Pat. No. 5,405,789 to Campbell et al., discloses construction of thermostable mutants of low molecular mass xylanase from *Bacillus circulans*. U.S. Pat. No. 5,759,840 to Sung et al., discloses modification of a family 11 xylanase from *Trichoderma reesei* to improve thermophilicity, alkalophilicity and thermostability as compared to the natural xylanase. U.S. Pat. No. 5,916,795 to Fulcunaga et al., discloses a thermostable xylanase from *Bacillus*. A publication entitled "Xylanase Treatment of Oxygen-Bleached Hardwood Kraft Pulp at High Temperature and Alkaline pH Levels Gives Substantial Savings in Bleaching Chemicals" to Shah et al., (2000, which is herein incorporated by reference) discloses treating oxygen delignified hardwood

pulp with xylanase from *Thermotoga maritima* at pH 10 and 90° C. and subsequently bleaching the pulp. These documents disclose using xylanases to enzymatically treat pulp prior to chemical bleaching.

[0018] Following peroxyacids or xylanase treatment, the next stage in a typical pulp bleaching process is usually bleaching with chlorine dioxide, chlorine or in some instances, a combination of chlorine dioxide and other oxidative bleaching agents. For example, the first chlorine dioxide stage in a chemical bleaching process is often called the D₀ or D100 stage. Subsequent chlorine dioxide bleaching stages are referred to as D₁, D₂ and so on. For mills that bleach pulp without an alkali-oxygen delignification stage, the D₀ stage is the first chemical bleaching stage. The D₀ stage is usually carried out at pH 1.5 to 3.0. In a small but decreasing number of mills, up to 30% to 50% chlorine gas may be added to ClO₂ in an effort to achieve a higher efficiency of lignin removal. Such a stage is referred to as a C_D stage. After a D₀ or C_D stage, the pulp is washed with water, and alkaline extracted. Alkaline extraction is carried out by adjusting the pH of the pulp to 9.0 to 12.0 with sodium hydroxide or sodium carbonate at a temperature between 60° C. to 120° C. for a period of 30 to 90 minutes. After the alkaline extraction stage, the pulp is washed with water. The chlorine dioxide bleaching stage, wash and alkaline extraction is repeated until the pulp is suitably bleached. In most cases, two to three rounds of bleaching, alternating between chlorine dioxide stages and alkaline extraction stages, is required before the pulp is suitably bleached.

[0019] U.S. Pat. No. 5,645,686 discloses a process for bleaching a chemical paper pulp by means of a sequence of treatment stages involving at least one stage with hydrogen peroxide and at least one stage with a peroxyacid. The patent also discloses a xylanase treatment stage in addition to the pulp bleaching sequence. The patent does not suggest treating pulp with a simultaneous xylanase treatment stage and peroxyacid stage.

[0020] While the xylanase treatments in pulp bleaching processes generally result in enhanced pulp bleaching compared to equivalent pulp bleaching processes that do not comprise xylanase treatment, there is a need in the art to increase the efficiency of the xylanase treatment. The pulp industry is under pressure to decrease the use of chlorine-containing bleaching chemicals, such as chlorine and chlorine dioxide, and thus, any method or process which can be integrated into a pulp bleaching process to reduce the use of chlorine-containing bleaching chemicals or the toxic effluents produced by the use of such chemicals would be an important and valuable asset to the pulp industry. The industry would also save money by using fewer chemicals such as, chlorine dioxide in bleaching stages, and sodium hydroxide and hydrogen peroxide in alkaline extraction stages. Improving the efficiency of xylanase treatment would address these concerns by further decreasing chemical usage.

[0021] There is a need in the art for novel methods and more efficient methods of bleaching pulp. Further, there is a need in the art for methods, or processes which can be integrated into existing pulp bleaching processes to increase the efficiency of the bleaching process and reduce the use of chlorine containing bleaching compounds or the toxic efflu-

ents produced by the use of such chemicals. There is also a need to save money by decreasing chemical usage.

[0022] It is an object of the invention to overcome drawbacks in the prior art.

[0023] The above object is met by a combination of the features of the main claims. The sub claims disclose further advantageous embodiments of the invention.

SUMMARY OF TEE INVENTION

[0024] The invention relates to methods of bleaching pulp. More specifically the invention relates to methods of bleaching pulp using xylanase, along with hydrogen peroxide, peracids, or a combination thereof.

[0025] According to the present invention, there is provided a method of bleaching chemical pulp comprising a bleaching stage which comprises at least one xylanase enzyme and an oxidizing chemical, said oxidizing chemical comprising hydrogen peroxide, one or more peracids, or a mixture of hydrogen peroxide and one or more peracids. The bleaching stage of the invention may take place at a pH between about 5.0 and about 9.0.

[0026] The present invention is also directed to the method as outlined above wherein the peracid is selected from the group consisting of peracetic acid, performic acid, peroxy-monosulfuric acid, peroxyphosphoric acid, peroxy-nitric acid, and a combination thereof. Preferably the peracid is peracetic acid, performic acid, or peroxy-monosulfuric acid.

[0027] The present invention also pertains to the method as defined above wherein the bleach stage is preceded by one or more alkaline oxygen delignification stages. Furthermore, the bleach stage may be preceded by an ozone-peracid treatment.

[0028] The present invention also embraces the method as defined above wherein the bleach stage is followed by a bleaching sequence. The bleaching sequence may comprise a chlorine dioxide bleach sequence and/or an oxygen-peracid bleach sequence.

[0029] The present invention also provides a method of reducing kappa number of a chemical pulp comprising:

[0030] i) exposing the chemical pulp to a bleaching stage comprising at least one xylanase enzyme and at least one oxidizing chemical, the oxidizing chemical comprising hydrogen peroxide, one or more peracids, or a combination of hydrogen peroxide and one or more peracids, to produce a treated pulp;

[0031] ii) washing the treated pulp; and

[0032] iii) bleaching the treated pulp using chlorine dioxide, ozone, oxygen peracid, alkaline extraction, or a combination thereof;

[0033] The present invention pertains to a method of reducing the amount of chlorine dioxide required during a bleaching sequence of a chemical pulp comprising:

[0034] iv) exposing the chemical pulp to a bleaching stage comprising at least one xylanase enzyme and at least one oxidizing chemical, the oxidizing chemical comprising hydrogen peroxide, one or more peracids, or a combination of hydrogen peroxide and one or more peracids, to produce a treated pulp;

[0035] v) washing the treated pulp; and

[0036] vi) bleaching the treated pulp using chlorine dioxide

[0037] Furthermore, the present invention provides a method of bleaching a chemical pulp comprising:

[0038] i) exposing the chemical pulp to a bleaching stage comprising at least one xylanase enzyme and peracetic acid, the bleaching stage at a pH between about 5.0 and about 9.0, and comprising 0.5 to about 5 kg/t pulp of peracetic acid, for about 20 to about 60 min at a temperature from about 40° C. to about 70° C., and with a pulp consistency between about 4% to about 12%, to produce a treated pulp

[0039] ii) washing the treated pulp; and

[0040] iii) bleaching the treated pulp using a chlorine dioxide bleach sequence.

[0041] The method of the invention is an improvement over the separate treatments of xylanase and peroxyacids. The method of the invention uses only one bleaching tower rather than two. Surprisingly, the presence of the hydrogen peroxide and peracids do not destroy the activity of the xylanase. The benefit that a mill obtains from the use of peracids with xylanase is greater than the benefit with peracids alone. This enables a mill to run a less costly bleaching operation, or to further decrease the usage of chlorine-containing bleaching chemicals.

[0042] The pulp bleaching method may be performed in a mill as part of a larger pulp bleaching process. Further, the chemical pulp may comprise kraft pulp, soda pulp or sulfite pulp.

[0043] Also according to the method of the present invention as defined above, the first bleaching step may be preceded by an alkaline oxygen delignification stage.

[0044] The xylanase may be selected from the group consisting of BioBrite™ EB or BioBrite™ UHB xylanases, which are commercially available from Iogen Corporation, wild-type *Trichoderma reesei* xylanase II, or any other xylanase(s) active at the conditions of the mild extraction stage.

[0045] This summary does not necessarily describe all necessary features of the invention but that the invention may also reside in a sub-combination of the described features.

DESCRIPTION OF THE FIGURES

[0046] FIG. 1 shows the effect of various bleaching treatments at either 60° C. or 75° C. on the final brightness of the pulp following a pulp bleaching sequence. Control ClO₂ treatment (□); peracetic acid treatment (pH 6.5; ◇); peracetic acid treatment (pH 9.8; ◆); xylanase (■); and xylanase and peracetic acid (▲).

[0047] FIG. 2 shows the effect of various bleaching treatments at either 60° C. or 75° C. on the final brightness of the pulp following a pulp bleaching sequence. Control ClO₂ treatment (◆); peroxy-monosulfuric acid treatment (pH 5.5; ■); peroxy-monosulfuric acid treatment (pH 6.5; □); peroxy-monosulfuric acid treatment (pH 9; ●); xylanase (▲); and xylanase and peroxy-monosulfuric acid (Δ).

DESCRIPTION OF PREFERRED EMBODIMENT

[0048] The invention relates to methods of bleaching pulp. More specifically the invention relates to methods of bleaching pulp using xylanase with hydrogen peroxide, peracids, or a combination thereof.

[0049] The following description is of a preferred embodiment by way of example only and without limitation to the combination of features necessary for carrying the invention into effect.

[0050] According to the present invention, there is provided a method of bleaching chemical pulp comprising a bleaching stage which comprises at least one xylanase enzyme and at least one oxidizing chemical, the oxidizing chemical comprising hydrogen peroxide, one or more peracids, or a mixture of hydrogen peroxide and one or more peracids.

[0051] By the term "chemical pulp" it is meant any type of virgin fiber, secondary fiber, woody or nonwoody fiber, softwood, hardwood or a mixture thereof which has been treated by chemical pulping such as, but not limited to, kraft pulp, soda pulp or sulfite pulp and is subsequently in a form suitable for bleaching. In a non-limiting example, the chemical pulp, comprises virgin fiber.

[0052] Chemical pulp also includes kraft pulp, soda pulp or sulfite pulp that has been exposed to an alkali oxygen delignification stage prior to practicing the method of the present invention. The alkaline oxygen delignification stage may be followed with a water-wash. Other conditions associated with the production of chemical pulp, including kraft and sulfite pulps are described in *Pulp Bleaching: Principles and Practice*, edited by Dence and Reeve, 1996 (which is herein incorporated by reference).

[0053] By the term "bleaching" it is meant contacting the pulp with one or more chemicals for a sufficient length of time and at the appropriate pH and temperature to effect a partial delignification and/or brightening of the pulp. Examples of chemicals that may be used for bleaching include but are not limited to ClO_2 , H_2O_2 , peracids, NO_2 or other chemicals as would be known to one of skill in the art.

[0054] The term "bleaching stage" is meant to convey the usual use of the term in the industry. This comprises a combination of piping, pumps, and chutes for conveying pulp from a washer to a bleach tower, the bleaching tower itself, and the piping, pumps, and chutes for conveying the pulp to the next washer for washing the solubilized chemicals out of the pulp. The bleaching stage of the present invention is preferably one of several bleaching stages in a mill. The bleaching stage as described herein may be preceded by one or more oxygen delignification stages. In this case, the bleaching stage as described herein may be placed at the end of a typical bleaching sequence, including, but not limited to, those using chlorine dioxide (CPPA Technical Section; Dence and Reeve, eds. 1996; which are both incorporated herein by reference), ozone, oxygen-peracid (Bouchard et al., 2001), alkaline extraction, or a combination thereof. Alternatively, the bleaching stage of the present invention may be carried out prior to a typical bleaching sequence. In this embodiment, the bleaching stage as described herein is followed by one or more chemical bleaching stages, including, but not limited to, chlorine dioxide, ozone, oxygen-peracid, alkaline extraction, or a combination thereof.

[0055] The xylanase enzyme present in the bleaching stage can be any xylanase that is capable of hydrolyzing xylan and enhancing the bleaching of pulp under the conditions that may be used in the method of the present invention. The xylanase must be active at the pH and temperature of the stage, and be resistant to the oxidizing chemicals that are present. The xylanase dosage is preferably from about 0.5 to about 2.0 xylanase units per gram of pulp. Methods of measuring xylanase units are described in Example 2.

[0056] Both wild-type and genetically modified xylanases may be employed in the method of the present invention. For example, but not wishing to be limiting, xylanases which may be useful in the method of the present invention include fungal xylanases which exhibit optimal activity at acidic pHs in the range of about 3.5 to about 5.5 and at temperatures of about 50° C., and bacterial xylanases which exhibit optimal activity at pH from about 5 to about 7 and temperatures between about 50° C. to about 70° C. However, it is to be understood that alternate xylanase enzymes may be used that exhibit varied temperature and pH profiles. In this case, the desired temperature and pH ranges will depend upon the xylanase enzyme used.

[0057] Therefore, the present invention contemplates using xylanase enzymes that may include, but are not limited to, wild-type, thermostable and allcalostable xylanases as taught in U.S. Pat. No. 5,405,789, which discloses mutants of low molecular mass from *Bacillus circulans*, and U.S. Serial No. 60/213,803 (PCT/CA/01/00769; which is herein incorporated by reference), which discloses xylanases having increased thermophilicity and alkalophilicity relative to the wild-type *Trichoderma* xylanase, for example but not limited to HTX-18 xylanase (commercially available from Iogen Corporation), or wild-type *Trichoderma reesei* xylanase II, for example but not limited to BioBrite™ (which is commercially available from Iogen Corporation), or modified *T. reesei* xylanase II, for example but not limited to EB xylanase (which is commercially available from Iogen Corporation). Further, other xylanases may be useful in the method of the present invention including thermostable xylanases such as *Caldocellum saccharolyticum*, *Thermotoga maritima* and *Thermotoga* sp. Strain FJSS-B.1 (Luithi et al., 1990; Winterhalter and Leibl, 1995; Simpson et al., 1991; which are herein incorporated by reference). The method of the present invention further contemplates the use of xylanases derived from, but not limited to *Trichoderma reesei* xylanase I, *Trichoderma viride* xylanase, *Streptomyces lividans* xylanase B, *Streptomyces lividans* xylanase C, or other non-family 11 xylanases, for example, but not wishing to be limiting, *Caldocellum saccharolyticum*, *Thermotoga maritima* and *Thermotoga* sp. Strain FJSS-B.1.

[0058] Genetically modified variants of xylanase also may be used in combination or alone in the enzyme treatment stages of the present invention provided they are capable of enhancing the bleaching of pulp, that is enhancing removal of lignin from pulp under the conditions of the subsequent bleaching stages. Genetically modified variants might have superior ability to act over a wider range of pH, temperature or concentration of oxidizing chemicals than the corresponding wild-type xylanase.

[0059] As is evident to someone of skill in the art, some native xylanases exhibit both xylanase and cellulase activi-

ties. The additional cellulolytic activity is undesirable for pulp bleaching due to its detrimental effect on cellulose, the bulk material in paper. It is preferred that the method of the present invention use one or more xylanases which lack cellulolytic activity or is reduced in cellulolytic activity. In a non-limiting example, the method of the present invention uses one or more xylanases that have reduced or impaired cellulase activity.

[0060] The term "oxidizing chemical" refers to a chemical that has the capability of bleaching the pulp, that is, partially delignifying, brightening, or both partially delignifying and brightening, the pulp. The oxidizing chemical is present at an amount, pH, and temperature at which it can bleach the pulp. Non-limiting examples of oxidizing chemicals include hydrogen peroxide and peracids.

[0061] In one aspect of the present invention, the bleaching stage comprises xylanase and an oxidizing chemical for example, hydrogen peroxide. The hydrogen peroxide may be present at a concentration of about 0.25 to about 10.0 kg/t pulp. For example, the hydrogen peroxide may be from about 0.25 to about 5 kg/t pulp. Below this concentration, hydrogen peroxide is ineffective at delignifying and/or brightening the pulp. Above this concentration, the hydrogen peroxide may damage the pulp. Hydrogen peroxide, when used in the absence of peracids, is added to the pulp in a manner familiar to those skilled in the art. Agents such as magnesium sulfate and sodium silicate may be added with the hydrogen peroxide to stabilize it and/or protect the cellulose and thereby the strength of the pulp.

[0062] In an alternate embodiment of the present invention, the bleaching stage may comprise xylanase along with one or more peracids (also referred to as peroxyacids) as oxidizing chemicals. Peracids are formed when hydrogen peroxide is added to an organic acid or an inorganic acid. The bleaching stage of the present invention may use a single peracid or it may use a mixture of peracids.

[0063] If the peracid is an organic acid, then non-limiting examples of peracids that may be used in accordance with the present invention include peracetic acid, performic acid, peroxymonosulfuric acid, peroxyphosphoric acid, peroxytrifluoroacetic acid, or a combination thereof. The one or more organic peracids can be, but is not limited to peracetic acid, performic acid or a combination thereof. Organic peracids may be present at a molar concentration of about twice to about ten times that of the hydrogen peroxide. More preferably, the one or more peracids is present from about 2 to about 5 times that of hydrogen peroxide. When used alone, the one or more peracids are present at about 0.5 to about 5 kg/t pulp.

[0064] If the peracid is an inorganic acid, then it is preferably peroxymonosulfuric acid, peroxytrifluoroacetic acid, peroxyphosphoric acid, or a combination thereof. The inorganic peracid is used at a molar concentration that is about 1 to 3 times that of the hydrogen peroxide. Combinations of organic and inorganic peracids may also be used within the bleaching stage as described herein.

[0065] The peracid can be made external to the bleach plant (for example as described in Spinger and McSweeney, 1993, which is incorporated herein by reference) and added directly to the pulp. This may be done by pumping aqueous solutions of the chemicals onto the pulp, preferably without

direct contact of the xylanase. Alternatively, the peracids can be generated in situ by adding hydrogen peroxide, and one or more acids, or other reactants, to the pulp and generating the peracids (for example as described in Christiansen et al., 1966, which is incorporated herein by reference). The pulp may already comprise xylanase, or the enzyme may be added after in situ generation of the one or more peracids.

[0066] A peroxide activator, for example but not limited to TAED (Tetra Acetyl Ethylene Diamine), may be reacted with hydrogen peroxide either before or during addition to the pulp (Turner and Mathews, 1998; which is incorporated herein by reference). The resulting product contains peracetic acid with or without hydrogen peroxide.

[0067] In another aspect of the present invention, the bleaching stage comprises a mixture of xylanase along with hydrogen peroxide and peracids as oxidizing chemicals. When used together, the hydrogen peroxide may be present at a concentration of about 0.25 to about 10.0 kg/t pulp, and the one or more peracids are present at a molar concentration from about two to about 10 times that of hydrogen peroxide. In a non-limiting example, the hydrogen peroxide is present from about 1 to about 5 kg/t pulp, and the one or more peracids is an organic peracid and at a molar concentration of about 1 to about 5 times that of hydrogen peroxide.

[0068] The combination of xylanase with, hydrogen peroxide, peracids, or both hydrogen peroxide and peracids, leads to an increased performance, in terms of Kappa number and pulp brightness, delignification, downstream bleach boosting, or a combination of these properties. This is in spite of the fact that combining xylanase with an aggressive bleaching chemical is generally thought to destroy the enzyme.

[0069] The bleaching stage may comprise xylanase and hydrogen peroxide, peracids, or both hydrogen peroxide and peracids, can be carried out at a pH of about 5.0 to about 9.0. For example, the bleaching stage of the invention takes place at a pH of about 6.5 to 8.0.

[0070] The bleaching stage as described herein may be carried out at a temperature of about 40° C. to about 70° C., or from about 50° C. to about 60° C., at a pulp consistency of about 4% to about 12%, and for a time of 20 to 60 minutes. However, longer treatment times may be used if desired.

[0071] The bleaching stage of the invention may comprise a water wash as a final step of the stage prior to the next step of bleaching the pulp. The bleaching stage of the present invention may be carried out before or after typical bleach sequences that include, but are not limited to, those using chlorine dioxide, ozone, alkaline extraction, oxygen-peracid treatment, or a combination thereof (see Pulp Bleaching: Principles and Practice, Chapter 4)

[0072] After the bleaching stage as described herein, the amount of lignin associated with pulp may be estimated by determining the kappa number of the pulp, which may be performed according to Example 1.

[0073] The pulp bleaching method of the present invention enhances the brightness, or decreases the kappa number, of the pulp when compared to conventional pulp bleaching processes known in the art. By enhancing brightness (or decreasing kappa number) less chemical treatment of the

pulp is required within the remainder of the bleaching sequence, resulting in a saving to the cost of bleaching, and the release of chemicals within the environment. For example, as shown in **FIG. 1**, the amount of ClO_2 required to bleach a pulp sample may be reduced by about 3.9% when peracetic acid is used within a bleaching stage, and the amount of ClO_2 may be reduced by about 13.6% when xylanase is used within a bleaching stage. The combination of both peracetic acid and xylanase within a bleaching stage as described herein, followed by a bleaching sequence, results in a reduction of ClO_2 addition of about 18.5%. A synergistic result, arising from the combination of xylanase and peracetic acid, is observed when the brightness (e.g. **FIG. 1**; Table 2, Example 6) or kappa number (e.g. Table 1, Example 5) of pulp is determined. **FIG. 2** shows that the amount of ClO_2 required to bleach a pulp sample may be reduced by about 0.27-0.81% when peroxymonosulfuric acid is used within a bleaching stage, and by about 12.4% when xylanase is used within a bleaching stage. A synergistic result is observed in the combination of peroxymonosulfuric acid and xylanase within a bleaching stage as described herein, followed by a bleaching sequence, as the amount of ClO_2 required is reduced by about 16.2%. A synergistic result, arising from the combination of xylanase and peroxymonosulfuric acid, is observed when the brightness (e.g. **FIG. 1**) or kappa number (e.g. Tables 1 and 2, Example 5, respectively) of pulp is determined.

[0074] The pulp bleaching method of the present invention may be easily integrated into pulp bleaching processes that are currently practised in the art. Existing pretreatment towers, for example towers that are currently used for xylanase treatment, may be adapted for use with hydrogen peroxide, one or more peracids, or a combination thereof and xylanase. Similarly, a bleaching tower used at the end of a bleaching sequence may be adapted for use for a bleaching stage as described herein.

[0075] The above description is not intended to limit the claimed invention in any manner. Furthermore, the discussed combination of features might not be absolutely necessary for the inventive solution.

[0076] The present invention will be further illustrated in the following examples. However, it is to be understood that these examples are for illustrative purposes only, and should not be used to limit the scope of the present invention in any manner.

EXAMPLE 1

Determination of Kappa Number

[0077] The kappa number of the pulp is determined using the protocol described in: TAPPI method for Kappa number of pulp (T 236 cm-85) from TAPPI Test Methods 1996-1997, which is herein incorporated by reference. Briefly, the kappa number is the volume (in milliliters) of a 0.1 N potassium permanganate solution consumed by one gram of moisture-free pulp under the conditions specified in the method. The results are corrected to 50% consumption of the permanganate added.

[0078] The kappa number determination is performed at a constant temperature of $25^\circ\text{C} \pm 0.2^\circ\text{C}$. with continuous agitation. However, it is possible to correct for variations in temperature as is described below.

[0079] The moisture content of the pulp is determined in accordance with TAPPI T 210 "Sampling and Testing Wood Pulp Shipments for Moisture" which is herein incorporated by reference. Briefly, the pulp specimen is disintegrated in about 800 mL of distilled water and stirred. 100 mL of 0.1 N potassium permanganate and 100 mL of 4N sulfuric acid (bringing the total volume to about 1 L) are added to the slurry and allowed to react for 10 minutes. At the end of the 10 minute period, the reaction is stopped by adding 20 mL of 1.0 N potassium iodide and the solution is titrated with 0.2 N sodium thiosulfate.

[0080] The kappa number of the pulp may be calculated using the following formula:

$$K = (p \times f) / w$$

wherein $p = (b - a)N / 0.1$

[0081] and wherein;

[0082] K is the kappa number;

[0083] f is the factor for correction to a 50% permanganate consumption, depending on the value of $p (f = 10^{(0.00093 \times (p - 50))})$;

[0084] w is the weight in grams of moisture-free pulp in the specimen;

[0085] p is the amount of 0.1 N potassium permanganate solution consumed by the test specimen in mL;

[0086] b is the amount of the thiosulfate solution consumed in a blank determination in mL;

[0087] a is the amount of thiosulfate solution consumed by the test specimen in mL; and

[0088] N = normality of the thiosulfate solution

[0089] Correction of the kappa number of the pulp for determinations made at temperatures between 20°C . and 30°C . maybe made using the formula:

$$K = p \times f (1 + 0.013(25 - t)) / w$$

[0090] wherein t is the actual reaction temperature in degrees Celsius.

EXAMPLE 2

Standard Assay for the Measurement of Xylanase Activity

[0091] Xylanase Assay #1:

[0092] The endo-xylanase assay is specific for endo-1,4-beta-D-xylanase activity. On incubation of azo-xylan (oat) with xylanase, the substrate is depolymerized to produce low-molecular weight dyed fragments which remain in solution on addition of ethanol to the reaction mixture. High molecular weight material is removed by centrifugation, and the colour of the supernatant is measured. Xylanase activity in the assay solution is determined by reference to a standard curve.

[0093] Substrate: The substrate is purified (to remove starch and beta-glucan). The polysaccharide is dyed with Remazolbrilliant Blue R to an extent of about one dye molecule per 30 sugar residues. The powdered substrate is dissolved in water and sodium acetate buffer and the pH is adjusted to 4.5.

[0094] Assay: Xylanase is diluted in 0.5 M acetate buffer at pH 4.5. Two millilitres of the solution is heated at 40° C. for 5 minutes. 0.25 mL of pre-heated azo-xylan is added to the enzyme solution. The mixture is incubated for 10 minutes. The reaction is terminated and high molecular weight substrate is precipitated by adding 1.0 mL of ethanol (95% v/v) with vigorous stirring for 10 seconds on a vortex mixer. The reaction tubes are allowed to equilibrate to room temperature for 10 minutes and are then centrifuged at 2000 rpm for 6-10 minutes. The supernatant solution is transferred to a spectrophotometer cuvette and the absorbance of blank and reaction solutions measured at 590 nm. Activity is determined by reference to a standard curve. Blanks are prepared by adding ethanol to the substrate before the addition of enzyme.

[0095] The following assay may also be used to quantify xylanase activity.

[0096] Xylanase Assay #2:

[0097] The quantitative assay determines the number of reducing sugar ends generated from soluble xylan. The substrate for this assay is the fraction of birchwood xylan that dissolves in water from a 5% suspension of birchwood xylan (Sigma Chemical Co.). After removing the insoluble fraction, the supernatant is freeze dried and stored in a desiccators. The measurement of specific activity is performed as follows: Reaction mixtures containing 100 μ L of 30 mg/mL xylan previously diluted in assay buffer (50 mM sodium citrate, pH 5.5 or the pH optimum of the tested xylanase), 150 μ L assay buffer, and 50 μ L of enzyme diluted in assay buffer were incubated at 40° C. (or the temperature optimum of the tested xylanase). At various time intervals 50 μ L portions are removed and the reaction is stopped by diluting in 1 mL of 5 M NaOH. The amount of reducing sugars is determined using the hydroxybenzoic acid hydrazide reagent (HBAH) (Lever, 1972, Analytical Biochem 47:273-279). A unit of enzyme activity is defined as that amount generating 10 μ mol reducing sugar in 1 minute at 40° C. (or at the optimum pH and temperature of the enzyme).

EXAMPLE 3

Preparation of Chlorine Dioxide

[0098] Chlorine dioxide was made in the lab by the standard procedure of passing a mixture of chlorine gas and nitrogen through a series of columns containing sodium chlorite, and collecting the evolved gas in cold water. The chlorine dioxide was stored refrigerated at a concentration of 10.4 grams per litre in water. Further details regarding the preparation of chlorine dioxide may be found in Chlorine Dioxide Generation published by Paprican, Pointe Claire, Québec (which is herein incorporated by reference).

EXAMPLE 4

Conventional Xylanase Treatment of Pulp

[0099] This is a procedure for carrying out conventional xylanase treatment, prior to bleaching of the pulp.

[0100] A 15 g pulp sample having a predetermined kappa number is adjusted to a consistency of 10% (wt/vol) with pulp filtrate and the pH of the pulp is adjusted between 6.2 and 6.8 with a 1 N solution of sulfuric acid. The pulp sample

is heated to 60° C. prior to adding BioBrite™ UHB xylanase (commercially available from Iogen Corporation). The enzyme is added to samples, and the pulp samples are incubated at 60° C. for 60 minutes at 10% pulp consistency. Following the incubation period the reaction is stopped by washing the pulp with 2 liters of tap water at 60° C. and allowing the samples to air dry overnight. Testing beforehand established that the overnight incubation did not increase the apparent effects by the enzyme.

[0101] The enzyme dose is 500 ml/t pulp, which corresponds to 5.0 units of xylanase activity (measured according to the first xylanase assay described in Example 2) per gram of pulp. For comparative purposes, control pulp samples were mock-treated under conditions lacking xylanase to facilitate comparison of the different bleaching sequences.

EXAMPLE 5

Xylanase Treatment in the Presence of Hydrogen Peroxide and Peracetic Acid

[0102] Hardwood kraft pulp from a mill in Quebec, (K=16.7) was treated as follows:

[0103] Control pulp: This pulp was treated as outlined in Example 4, however, there was no addition of xylanase or oxidizing chemicals.

[0104] Xylanase-treated pulp: This pulp was treated with xylanase as described in Example 4.

[0105] Hydrogen peroxide treated pulp: This pulp was bleached with 0.045% hydrogen peroxide on pulp. The pulp was treated as outlined in Example 4, however, the hydrogen peroxide was added after the pH of the pulp was adjusted, and no xylanase was added.

[0106] Xylanase with hydrogen peroxide treated pulp: This pulp was treated as outlined in Example 4, however, following pH adjustment of the pulp, 0.045% hydrogen peroxide was added to the pulp, followed by the addition of xylanase.

[0107] Peracetic acid/Hydrogen peroxide treatment: A mixture of peracetic acid and hydrogen peroxide was made by combining an aqueous solution of 34% hydrogen peroxide, glacial acetic acid, and concentrated sulfuric acid in a ratio of 3.5:1.0:0.3. The reactants were combined at ambient temperature and allowed to sit for 60 minutes, then refrigerated. After one month of storage, the concentration of hydrogen peroxide was measured by the method of Swern (1970), which involves titration of the sample with ammonia ceric sulfate. The hydrogen peroxide concentration was determined to be 47.6 g/L. The concentration of peracetic acid was then measured by the method of Greenspan (1948), which involves titration of the sample with iodide. The peracetic acid concentration was determined to be 158.4 g/L. The peracetic acid/hydrogen peroxide mixture was added to the pulp such that the concentration of peracetic acid on pulp was 0.15% and the concentration of hydrogen peroxide on pulp was 0.045%. The pH of the pulp was adjusted to pH 6.2 to 6.8 with sodium hydroxide. The pulp was otherwise treated as outlined in example 4, except that no xylanase was added to the pulp

[0108] Xylanase, peracetic acid, and hydrogen peroxide: In this pulp treatment, peracetic acid and hydrogen peroxide

were added to the pulp as outlined above (Peracetic acid/Hydrogen peroxide treatment), and the pH of the pulp was adjusted to pH 6.2-6.8 with sodium hydroxide. Xylanase was added after the pH adjustment step. The pulp was otherwise treated as outlined in Example 4.

[0109] After all treatments, the pulp was washed with water and the kappa number measured according to Example 1. The results are shown in Table 1.

TABLE 1

The effect of various bleaching stage treatments on the kappa number of pulp. No further bleaching of the pulp was carried out.	
Treatment	K
Untreated	16.6, 16.7
Xylanase (500 ml/t)	15.2, 15.1
Hydrogen peroxide (0.045%)	16.6, 16.6
Xylanase + H ₂ O ₂	15.1, 15.0
Peracetic acid (0.15%) + H ₂ O ₂ (0.045%)	16.1, 16.2
Xylanase + Peracetic acid + H ₂ O ₂	14.8, 14.9

[0110] The xylanase addition decreased the kappa number (K) of the pulp by about 1.5 units. Under the present conditions, hydrogen peroxide was ineffective at delignifying the pulp. However, the combination of xylanase and hydrogen peroxide decreased the K by 1.6 units. This is slightly greater than the effect by xylanase alone and shows that the xylanase was still effective in the presence of the hydrogen peroxide.

[0111] Peracetic acid with hydrogen peroxide decreased the K by about 0.5 units. However, the combination of xylanase with peracetic acid and hydrogen peroxide decreased the K by 1.8 units, which is greater than the effect by peracetic acid with hydrogen peroxide, and greater than the effect by xylanase alone. These results demonstrate a synergistic effect of combining xylanase, peracids and hydrogen peroxide. Furthermore, these results demonstrate that xylanase is effective in the presence of peracetic acid and hydrogen peroxide.

EXAMPLE 6

Xylanase and Peracetic Acid Treatment of Pulp Partially Bleached with ClO₂

[0112] Hardwood pulp taken from the D₁ stage of an eastern Canadian pulp mill was treated as follows:

[0113] Control pulp. This pulp sample was treated as described in Example 4, but without the addition of xylanase. Also, the pH was adjusted to 6.5 with sodium carbonate (to prevent alkali-induced brightness reversion) rather than sulfuric acid.

[0114] Xylanase treatment This pulp was treated with xylanase as outlined in Example 4, with an enzymed dosage of 150 mL/t, except that the pH was adjusted to 6.5 using sodium carbonate rather than sulfuric acid.

[0115] Peracetic acid treatment. The pulp was treated as outlined in Example 4, but without xylanases being added. Also, the pH of the pulp was adjusted to 6.5 with sodium carbonate rather than sulfuric acid, then 1 kg peracetic acid was added per ton of pulp.

[0116] Xylanase and peracetic acid treatment. The pulp was treated with xylanase as described in Example 4, with an enzyme dosage of 150 mL/t, except that the pH of the pulp was adjusted to 6.5 with sodium carbonate rather than sulfuric acid, then 1 kg peracetic acid was added per ton of pulp.

[0117] Following all treatments, the pulp was washed with water and the brightness of the pulp was measured according to the procedures of Example 8. The results are presented in Table 2.

TABLE 2

The effect of xylanase and peracetic acid treatment on pulp partially bleached with ClO ₂ . No further bleaching of the pulp was carried out.	
Treatment	Brightness (% ISO)
Control	84.5
Xylanase (150 mL/t)	86.0
Peracetic acid (1 kg/t)	86.4
Xylanase + peracetic acid	86.6

[0118] The xylanase treatment increased the brightness 1.5 units over the control whereas peracetic acid increased the brightness 1.9 units over the control, indicating that peracetic acid is more effective than xylanase. The xylanase+peracetic acid treatment gave the largest increase, 2.1 units. The combination of xylanase and peracetic acid shows a synergistic effect in increasing the brightness of partially bleached pulp compared to xylanase or peracetic acid alone.

EXAMPLE 7

Chlorine Dioxide Bleaching of Hardwood Pulp Samples

[0119] Pulp samples are subjected to chlorine dioxide bleaching stages which are similar to those described in Glossary of Bleaching Terms CPPA technical section (which is herein incorporated by reference), using optimum conditions of 1.0%-2.3% ClO₂ on pulp, 40° C.-60° C., 3-10% pulp consistency, 30-60 minute incubation period, pH 2.5 to 3.0.

[0120] The pulp was hardwood craft pulp from a mill in the western US, with a K=15.0.

[0121] Chlorine Dioxide Bleaching (Do) Stage

[0122] The first chlorine dioxide bleaching stage is the Do stage. ClO₂ is added to the pulp and the system is maintained in a heat-sealable plastic bag. The pulp mixture is cooled to 4° C. to minimize evaporation. Pulp kappa factors of 0.194, 0.217, 0.239 and 0.262 were used to calculate the chlorine dioxide charge required in the bleaching stage. The chlorine dioxide charge may be determined using the following formula:

$$\text{Chlorine dioxide charge (kg/ton pulp)} = 10 \times \text{kappa factor} \times \text{kappa number} / 2.63$$

[0123] Based on a kappa factor of 0.194 and a pulp kappa number of 15.0, the corresponding chlorine dioxide usage is 11.1 kg/tonne pulp. After ClO₂ addition, the pulp comprises 4% consistency, pH 2.5 to 3.0 and the bags are placed in a 50° C. water bath for 60 minutes. Following the incubation period, pulp samples are washed with 2L of tap water.

Subsequently, Do pulp samples are subjected to a conventional alkaline extraction stage (Eop).

[0124] Alkaline Extraction Stage (Eop)

[0125] After the first chlorine dioxide bleaching stage (Do), the pulp samples are subjected to an alkaline extraction stage (Eop). The Eop stage comprises incubating pulp samples at 77° C., 10% (wt/vol) consistency, with a sodium hydroxide charge of 1.4%, a hydrogen peroxide charge of 0.65% (wt/wt) and an oxygen pressure of 5 psig, to consume 6 kg oxygen per tonne pulp, for 90 minutes. The pH of the extraction medium is about 11.0 at the end of the incubation. Following the incubation period, each pulp sample is washed with 2L of tap water.

[0126] Chlorine Dioxide Bleaching (D₁) Stage

[0127] After the extraction stage, all pulps are subjected to D₁ stages. The D₁ stage is performed in a generally similar manner to the Do stage. Briefly, pulp samples are adjusted to a consistency of 10% (wt/vol) and incubated at pH 3.6 to about 4, 75° C. for 180 minutes. The D₁ chlorine dioxide charges are chosen to correspond with kappa factors of 0.09, 0.101, 0.111, and 0.122 corresponding to the order of pulps, from lowest to highest kappa factor, in the Do stage. Following the incubation period, each pulp sample is washed with 2L of tap water. Following the extraction the brightness of the pulp may be measured according to Example 8. This is the D₁ brightness of the pulp.

EXAMPLE 8

Measuring Pulp Brightness

[0128] Pulp brightness is measured according to the method disclosed by PAPTAC-Standard Testing Methods July, 1997 (Standard E1 brightness of Pulp, Paper and Paperboard; which is herein incorporated by reference). Briefly, a 3.75 g sample of oxygen delignified pulp is used to form a brightness pad. A pulp sample is placed in a 500 mL container and water is added to about 200 mL. About 2 mL of sulfuric acid solution is added to each jar and the contents mixed well. A pad is formed pouring the pulp into a funnel under vacuum and subsequently pressing the pad with a plunger. Each pad is pressed between blotters using a hydraulic press. The pulp pad is allowed to dry overnight at room temperature.

[0129] ISO Brightness Determination

[0130] Brightness is measured using an Elrephometer. The sample is diffusely illuminated using a highly reflecting, integrated sphere. Reflected light is measured at right angles to the sample. Reflectance is compared to absolute reflectance based on a perfectly reflecting, perfectly diffusing surface that is considered to exhibit a brightness of 100%. Magnesium oxide is one standard that is used to compare to pulp brightness. A blue light of wavelength 457 nm is used for the brightness reading.

EXAMPLE 9

Pulp Bleaching Experiments Using Xylanase Treatment in the Presence of Peracetic Acid

[0131] Hardwood kraft pulp from a mill in the western United States, (K=15.0) was treated as follows:

[0132] Control pulp. This pulp was treated as described in Example 4, except that no xylanase was added. Furthermore,

the method of Example 4 was modified in that the treatment procedure was carried out at 75° C., and at a pH 9.8, for 1 hour.

[0133] Xylanase-treated pulp. This pulp was treated with xylanase as described in Example 4, with an enzyme dosage of 150 ml/t, at 60° C., pH 6.5 for 1 hour.

[0134] Peracetic acid treatment, pH 9.8. This pulp was treated as outlined in Example 4, however, a mixture of hydrogen peroxide and tetra-acetyl ethylene diamine (TAED) was added after the pH adjust step. Furthermore, the pH of the pulp was adjusted to pH 9.8 using dilute sodium hydroxide, and the pulp was incubated for 1 hour at 75° C. The hydrogen peroxide and TAED mixture was made at a concentration of 0.34 g hydrogen peroxide and 1.14 g TAED in 100 ml deionized water. The mixture was adjusted to pH 7 with 10% sodium hydroxide and heated gently to dissolve the TAED. Once the TAED dissolved, the solution was allowed to stand for 15 minutes. At this point, the titration method of Swern (1970) indicated that the hydrogen peroxide concentration was below the limits of detection. The titration method of Greenspan (1948) indicated that the peracetic acid concentration was 6.6 grams/liter. The solution was stored refrigerated. The peracetic acid was added to the pulp at a level of 0.1% on pulp.

[0135] Peracetic acid treatment, pH 6.5. This pulp is treated with peracetic acid as outlined above (peracetic acid treatment, Example 9). However the pulp is incubated at 60° C., pH 6.5

[0136] Xylanase with peracetic acid. This pulp sample is treated as outlined in example 4, however peracetic acid, prepared as outlined above (peracetic acid treatment, Example 9), was added to the pulp after the pH of the pulp was adjusted to pH 6.5 with sodium hydroxide, followed by the addition of xylanase at an enzyme dosage of 150 ml/t. The treatment was carried out at 60° C., pH 6.5 for 1 hour.

[0137] After all the treatments described above, the pulp was washed with water and then bleached DoEopD₁ as described in Example 7. Following bleaching, the brightness of the pulp was measured according to the procedures of Example 8. The results are shown in **FIG. 1**.

[0138] The brightness target is 87.5 ISO. The untreated control pulp requires 20.6 kg/t of ClO₂ to reach this brightness level.

[0139] The xylanase treatment alone decreased the amount of ClO₂ to bleach the pulp to 87.5 brightness to 17.8 kg/t, a reduction of 13.6%. This is consistent with published reports on the benefits of xylanase treatment in ClO₂ bleaching.

[0140] Peracetic acid at its optimum pH (9.8) was effective in decreasing the amount of ClO₂ required to bleach the pulp to 18.1 kg/t, a reduction of 12.1%. The savings in ClO₂ of 2.5 kg/t with a 1 g/t peracetic acid treatment is consistent with published reports of the effects of peracetic acid in bleaching pulp.

[0141] Peracetic acid at a sub optimal pH (6.5) was less effective at decreasing ClO₂ usage. The savings in ClO₂ with this treatment was only 3.9%.

[0142] The combination of xylanase and peracetic acid decreased the ClO₂ required to bleach the pulp by 18.5%.

This is more effective than the xylanase or the peracetic acid alone. This indicates the large ClO_2 savings that are possible using a combination of xylanase and peracetic acid.

EXAMPLE 10

Pulp Bleaching Experiments Using Xylanase Treatment in the Presence Peroxymonosulphuric Acid (Oxone®)

[0143] Hardwood kraft pulp from a mill in western United States ($K=16.59$) was treated as follows:

[0144] Control pulp. This pulp was treated as described in Example 4, but without the addition of xylanase.

[0145] Xylanase-treated pulp. This pulp sample was treated with xylanase as described in Example 4, with an enzyme dosage of 150 mL/t.

[0146] Peroxymonosulphuric acid (Oxone®) treatment, pH 5.5. This pulp was treated as outlined in Example 4, but without the addition of xylanases. Also, 4 kg Oxone® (a peroxymonosulphate complex, Sigma-Aldrich, St. Louis, Mo.) per ton of pulp was added following adjustment of the pulp pH to 5.5.

[0147] Peroxymonosulphuric acid (Oxone®) treatment, pH 6.5. This pulp was treated as outlined in Example 4, but without the addition of xylanases. Also, 4 kg Oxone® per ton of pulp was added following adjustment of the pulp pH to 6.5.

[0148] Peroxymonosulphuric acid (Oxone®) treatment, pH 9. This pulp was treated as outlined in Example 4, but without the addition of xylanases. Also, 4 kg Oxone® per ton of pulp was added following adjustment of the pulp pH to 9, and the sample was incubated at 75° C.

[0149] Xylanase with Peroxymonosulphuric acid (Oxone®). This pulp sample was treated as outlined in Example 4, with an enzyme dosage of 150 mL/t, except that 4 kg Oxone® per ton of pulp was added following adjustment of the pulp pH to 6.5.

[0150] After all the treatments described above, the pulp was washed with water and then bleached $D_0E_{OP}D_1$ as described in Example 7. For the D_0 stage kappa factors of 0.277, 0.249 and 0.222 were used for the Control pulp. For the other pulps D_0 kappa factors of 0.249, 0.222 and 0.193 were used. All D_0 samples were incubated at a consistency of 4.3%, 66° C. and 40 minutes. The E_{OP} conditions for all pulp samples were: 77° C., 10% consistency, sodium hydroxide charge of 1.5-2.2%, hydrogen peroxide charge of 0.75%, 0.6% oxygen and an incubation time of 90 minutes. For the D_1 stage kappa factors of 0.146, 0.132 and 0.117 were used for the Control pulp, and kappa factors of 0.132, 0.117 and 0.103 for the other pulps. Following bleaching, the brightness of the pulp was measured according to the procedures of Example 8. The results are presented in FIG. 2.

[0151] The brightness target was 89% ISO. The Control pulp required 23.4 kg/t of ClO_2 to reach this brightness level.

[0152] The xylanase-treated pulp required 20.5 kg/t ClO_2 to bleach the pulp to 89% ISO, a reduction of 12.4%.

[0153] Pulp submitted to peroxymonosulphate (Oxone®) treatment at pH 5.5, pH 6.5 and pH 9 required 23.3 kg/t, 23.2

kg/t and 23.3 kg/t of ClO_2 respectively to reach the brightness level of 89%, reductions of only 0.27%, 0.81% and 0.54% respectively.

[0154] Pulp treated with xylanase and Peroxymonosulphate (Oxone®) required 19.6 kg/t of ClO_2 to reach the brightness level of 89%, corresponding to a 16.2% reduction in the amount of ClO_2 . This is more effective reduction than xylanase or Oxone® alone, indicating large CNO, savings are possible using a combination of xylanase and peroxymonosulphate.

[0155] All references are herein incorporated by reference.

[0156] The present invention has been described with regard to preferred embodiments. However, it will be obvious to persons skilled in the art that a number of variations and modifications can be made without departing from the scope of the invention as described herein.

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The embodiments of the invention in which an exclusive property of privilege is claimed are defined as follows:

1. A method of bleaching chemical pulp comprising, exposing said chemical pulp to a bleaching stage comprising at least one xylanase enzyme and at least one oxidizing chemical, said oxidizing chemical comprising hydrogen peroxide, one or more peracids, or a mixture of hydrogen peroxide and one or more peracids.

2. The method of claim 1, wherein said bleaching stage takes place at a pH between about 5.0 and about 9.0.

3. The method of claim 2 wherein said peracid is selected from the group consisting of peracetic acid, performic acid, peroxymonosulfuric acid, peroxyphosphoric acid, peroxynitric acid, and a combination thereof.

4. The method of claim 3 wherein said peracid is peracetic acid or performic acid.

5. The method of claim 3 wherein said peracid is peroxymonosulfuric acid.

6. The method of claim 3 wherein said peracid is produced external to said bleaching stage, and then is added to said bleaching stage.

7. The method of claim 3 wherein said peracid is produced within said bleaching stage.

8. The method of claim 3 wherein said bleaching stage is conducted for a period of 20 to 60 minutes at a temperature of: about 40° C. to about 70° C., and at a pulp consistency of about 4% to about 12%.

9. The method of claim 1, wherein said chemical pulp comprises kraft pulp, soda pulp or sulfite pulp.

10. The method of claim 1, wherein said method is performed in a pulp mill.

11. The method of claim 3 wherein said pH is between about 6.5 to about 8.

12. The method of claim 1 wherein said xylanase is selected from the group consisting of BioBrite™ EB xylanase, HTX-18, and wild-type *Trichoderma reesei* xylanase II.

13. The method of claim 1 wherein said bleach stage is preceded by one or more alkaline oxygen delignification stages.

14. The method of claim 1 wherein said bleach stage is preceded by an ozone-peracid treatment.

15. The method of claim 1 wherein said bleach stage is followed by a bleaching sequence.

16. The method of claim 15, wherein said bleaching sequence comprises a chlorine dioxide bleach sequence.

17. The method of claim 15, wherein said bleaching sequence comprises an ozone-peracid bleach sequence.

18. The method of claim 1 wherein said oxidizing chemical is hydrogen peroxide, said hydrogen peroxide present at an amount of between about 1 and about 10 kg per tonne pulp.

19. A method of reducing kappa number of a chemical pulp comprising:

vii) exposing said chemical pulp to a bleaching stage comprising at least one xylanase enzyme and at least one oxidizing chemical, said oxidizing chemical comprising hydrogen peroxide, one or more peracids, or a combination of hydrogen peroxide and one or more peracids, to produce a treated pulp;

viii) washing said treated pulp; and

ix) bleaching said treated pulp using chlorine dioxide, ozone, oxygen peracid, alkaline extraction, or a combination thereof;

20. A method of reducing the amount of chlorine dioxide required during a bleaching sequence of a chemical pulp comprising:

x) exposing said chemical pulp to a bleaching stage comprising at least one xylanase enzyme and at least one oxidizing chemical, said oxidizing chemical comprising hydrogen peroxide, one or more peracids, or a combination of hydrogen peroxide and one or more peracids, to produce a treated pulp;

xi) washing said treated pulp; and

xii) bleaching said treated pulp using chlorine dioxide

21. A method of bleaching a chemical pulp comprising:

i) exposing said chemical pulp to a bleaching stage comprising at least one xylanase enzyme and peracetic acid, said bleaching stage at a pH between about 5.0 and about 9.0, and comprising 0.5 to about 5 kg/t pulp of peracetic acid, for about 20 to about 60 min. at a temperature from about 40° C. to about 70° C., and with pulp consistency between about 4% to about 12%, to produce a treated pulp

iv) washing said treated pulp; and

v) bleaching said treated pulp using a chlorine dioxide bleach sequence.

22. The method of claim 21, wherein in said step of exposing (step i)), said pH is about 6.5.

23. The method of claim 22, wherein in said step of exposing (step i)), said temperature is about 60° C.

24. The method of claim 22, wherein in said step of exposing (step i)), said pH of said chemical pulp is set, followed by addition of said peracetic acid, followed by addition of said xylanase.

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