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(71) Applicant (for all designated States except US): **INTERNATIONAL PAPER COMPANY** [US/US]; 6400 Poplar Avenue, Memphis, TN 38197 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **YIN, Caifang** [US/US]; 4837 Hampton Pond Lane, Mason, OH 45040 (US). **TREPOW, Alfred** [PL/PL]; Brzechwy 2/34, PL-85-792 Bydgoszcz (PL). **KALKA, Jacek** [PL/PL]; Baczynskiego 4/8, PL-82-500 Kwidzyn (PL). **GOYAL, Gopal** [US/US]; 7838 Plumfield Court, Mason, OH 45040 (US).

(74) Agents: **ECKERT, Inger, H.** et al.; International Paper Company, 6285 Tri-Ridge Boulevard, Loveland, OH 45140 (US).

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(54) Title: EFFECT OF LOW DOSE XYLANASE ON PULP IN PREBLEACH TREATMENT PROCESS

(57) Abstract: A prebleach treatment of pulp with xylanase enzyme prior to chemical bleaching is disclosed. A process of making pulp comprises treating a pulp with xylanase in an amount of less than 50g of xylanase per ton of pulp. The treating step is carried while buffering the pulp and xylanase with a buffering agent to a pH of from about 6.5 to about 7.5 prior to at least one bleaching stage to form a treated pulp.



EFFECT OF LOW DOSE XYLANASE ON PULP IN PREBLEACH TREATMENT PROCESS

FIELD OF THE INVENTION

This invention relates generally to a pre-bleaching treatment of pulp. More particularly, the invention relates to the effect of low dose Xylanase on pulp in pre-bleach treatment process.

BACKGROUND OF THE INVENTION

Xylanases are used in the pulp and paper industry to enhance the bleaching of pulp and to decrease the amount of bleaching chemicals used in bleaching stages. There have been several mechanisms proposed for the bleaching action of xylanase. One mechanism is that lignin is attached 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, sodium hydroxide, hydrogen peroxide, or combinations of these chemicals to bleach pulp more efficiently than in the absence of xylanase. Pretreatment of pulp with xylanase prior to chemical bleaching increases the brightness and quality of the final paper product and reduces the amount of chlorine-based chemicals which must be used to bleach the pulp. This in turn decreases the chlorinated effluent produced by such processes.

A group of xylanase enzymes produced from fungi or bacteria have been practiced by paper industry for pulp prebleaching. It has been demonstrated that using xylanase enzymes in

pulp prebleaching reduces total ClO_2 consumption by about 10-15% along with a proportional decrease in the caustic usage. Many paper mills have been taking advantage of this non-capital approach to minimize the impact of rising chemical price on the profit.

The conventional practice of enzyme however causes a number of the problems that can deter this practice at the paper mills. These include: excessive yield loss, a significant increase (20-50%) in effluent Chemical Oxygen Demand (COD) loading to the Waste Water Treatment Plant (WWTP), interference with wastewater treatment biological activity, an increase in final effluent COD discharge, and potential impact on paper machine "sizing" chemistry.

These drawbacks particularly the effluents COD increase have largely prevented many paper mills from using the enzyme technology for bleaching cost reduction. For example, the xylanase usage has caused a 20,000 lb/day Biochemical Oxygen Demand (BOD) increase on HardWood (HW) pulp, responsible for the Waste Water Treatment Plant odor complaints in one paper mill. The increase in the effluent COD and its negative impact on the WWTP operation is also a deterrent to usage of Luminase enzyme application at another mill.

These challenges have led to intensive investigation to seek ways to use xylanase enzyme for effective reduction of bleaching chemicals without causing a significant increase in COD loading and interference with WWTP operation.

Therefore, there is a need in the art for methods or processes of prebleach treatment of pulp with xylanase enzyme prior to chemical bleaching.

SUMMARY OF THE INVENTION

The problems were successfully resolved by simultaneous deployment of the following key strategies in the present invention. The low enzyme dosage is the key factor one out of the three strategies.

Application of a catalytic enzyme dosage (up to 30 mg/l) made possible by the following improved strategies in enzyme treatment:

1. Selecting more efficient luminase xylanase enzyme.
2. Installing bleach plant prewasher to recycle enzyme.
3. Reducing pulp COD carryover with CO₂ improved washing.
4. Maintaining good pulp and enzyme mixing.
5. Improved pH control with CO₂.
6. Decreased Do and Eop delignification stage pH and temperature made possible by improved bleachability of enzyme pretreatment.
7. Adjustment in wastewater treatment operation parameters mainly increasing dissolved oxygen (DO) and macronutrients nitrogen and phosphorus (N and P) levels in proportion to any increase in wastewater organic (BOD) concentration as a result of enzyme treatment.

One aspect of this invention relates to prebleach treatment of pulp with xylanase enzyme prior to chemical bleaching. The unbleached pulp is treated with luminase xylanase up to an amount of about 10-50 g of luminase xylanase per ton of unbleached pulp to enhance subsequent bleaching of the unbleached pulp. The treatment of unbleached pulp is carried out while buffering the unbleached pulp and luminase xylanase with carbon dioxide to a pH of from about 6.5 to about 7.5.

Another aspect of this invention relates to a pulp bleaching system having a prebleach treatment of pulp which comprises unbleached pulp and luminase xylanase in an amount from about 10g to about 13 g per ton of unbleached pulp to enhance subsequent bleaching of the unbleached pulp and carbon dioxide buffering to provide a pH in the prebleach treatment stage from about 6.5 to about 7.5.

The process of the present invention provides one or more advantages over prior processes. For example, advantages of some of the embodiments of the process of this invention include 1) reduction of bleaching chemicals such as, ClO_2 , H_2O_2 , NaOH , H_2SO_4 or any combination of the foregoing, 2) reducing the bleaching cost, 3) reduce steam (energy) consumption, 4) reduce wastewater cooling cost, 5) minimize pulp yield loss, 6) minimize wastewater organic Chemical Oxygen Demand (COD) loading increase to WWTP, 7) improve WWTP efficiency, 8) decrease final effluent COD discharge, 9) minimize the potential impact on paper machine sizing chemistry, 10) high pulp brightness and brightness stability, and/ or 11) a combination of two or more of the aforementioned advantages. Some embodiments of this invention may exhibit one of the aforementioned advantages while other preferred embodiments may exhibit two or more of the foregoing advantages in any combination.

In this process of invention, a low dosage of luminase xylanase is required in the prebleach treatment of pulp as compared to conventional usage of xylanase in treating pulp that use a higher dosage followed by improved mixing and pH control using acids including carbon dioxide as buffering agent to provide a pH in the prebleach treatment stage from about 6.5 to about 7.5.

DETAILED DESCRIPTION OF THE INVENTION

While this invention is susceptible of embodiment in many different forms, there is shown and described in tables and examples and will herein be described in detail preferred embodiments of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspect of the invention to the embodiments illustrated.

It is advantageous to define several terms before describing the invention. It should be appreciated that the following definitions are used throughout this application.

Definitions

Where the definition of terms departs from the commonly used meaning of the term, applicant intends to utilize the definitions provides below, unless specifically indicated.

For the purpose of the present invention, 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. Preferably, the chemical pulp comprises virgin fiber. Chemical pulp also includes Kraft pulp, soda pulp or sulfite pulp which has been exposed to an alkali oxygen delignification stage prior to practicing the method of the present invention. 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).

For the purpose of the present invention, the term "**Xylanases**" has been isolated from a variety of organisms including bacteria and fungi. Xylanase has proven to be a valuable enzyme

for the pre-bleaching of pulp to enhance delignification of wood pulp by facilitating the removal of lignin from pulp. Therefore, xylanase prebleaching results in the use of lower amounts of bleaching chemicals as compared to nonenzymatic bleaching.

For the purpose of the present invention, the term “**Bleaching**” refers to whitening process carried out on pulps by selective chemical removal of residual lignin and other colored materials, and with minimal degradation of the cellulosic constituents. With respect to secondary fibers, bleaching can also have a dye removal function.

For the purpose of the present invention, the term “**Bleaching Chemical**” refers to a variety of chemical used in the bleaching of wood pulp such as chlorine (Cl_2), sodium hypochlorite (NaOCl), calcium hypochlorite [$\text{Ca}(\text{OCl})_2$], chlorine dioxide (ClO_2), sodium hydroxide, peroxide (H_2O_2), sodium chlorite (NaClO_2), Oxygen (O_2), Ozone (O_3) and others.

For the purpose of the present invention, the term “**Bleaching Sequence**” refers to series of stages, each with specific objectives (e.g., delignification, solubilization, destruction of chromophoric groups), that contribute to an overall whitening effect. Typically the pulp is washed between stages.

For the purpose of the present invention, the term “**Kappa Number**” refers to modified permanganate test value on pulp which has been corrected to 50% consumption of chemical. Kappa number has the advantage of a linear relationship with lignin content over a wide range. For pulp samples under 70% yield, the percent Klason lignin is approximately equal to the Kappa number times a factor of 0.15.

For the purpose of the present invention, the term “**Buffer**” refers to chemical solution that lower pH when acids are added. Such acids include, but not limited to, CO_2 , and H_2SO_4 .

For the purpose of the present invention, the term “**Buffering Action**” refers to ability to neutralize acids and bases as they are formed during a chemical reaction and thus resist a change in pH.

For the purpose of the present invention, the term “**Oxygen Delignification (O-Stage)**” refers to treatment of pulp in alkaline medium with oxygen to degrade and solubilize lignin, typically employed as the first stage of a bleaching sequence or as a bleaching “pre-stage”. The process is generally carried out at “medium consistency”. Oxygen is added as a gas and magnesium salts are usually employed as an additive to “protect” the cellulose from degradation.

For the purpose of the present invention, the term “**Chlorine dioxide (D) Stages**” refers to initial delignifying stage (D_0) and/or brightening stages (D_1 and D_2) in a bleaching sequence used to produce high-brightness pulp. Traditionally, the highest and most stable brightness (especially for the softwood Kraft pulps) is achieved when at least one chlorine dioxide (D) brightening stage is used with an alkaline extraction in between.

For the purpose of the present invention, the term “**Alkaline Extraction Stage-(E-Stage)**” refers to essential stage in any multistage bleaching sequence; it solubilizes the dark-colored chlorinated and / or oxidized lignin compounds formed in the initial acid delignification stage (e.g., chlorination or chlorine dioxide) and in later stages. When used prior to the final bleaching stage, an E-stage also serves to “activate” the pulp for more effective brightening.

For the purpose of the present invention, the term “**Peroxide Extraction Stage-(Ep-Stage)**” refers to alkaline extraction stage supplemented with a peroxide agent.

For the purpose of the present invention, the term “**Oxidative Extraction Stage-(Eo-Stage)**” refers to alkaline extraction stage supplemented with an oxidizing agent, most

commonly oxygen. Peroxide or hypochlorite may also be used as supplemental chemicals to provide a brightening effect and/or to reduce effluent color.

For the purpose of the present invention, the term “**Oxidative peroxide Extraction Stage-(Eop-Stage)**” refers to alkaline extraction stage supplemented with peroxide and an oxidizing agent.

For the purpose of the present invention, the term “**Brightening**” refers to 1) any chemical treatment to pulp that increases its brightness. 2) Chemical modification of colored elements in high-yield pulps to render them colorless without removing them, thus retaining the yield advantage of these pulps.

For the purpose of the present invention, the term “**Chemical Oxygen Demand (COD)**” refers to rapid chemical test to determine the oxygen demand of all organic matter present in a sample of wastewater. The limitation of the test is its inability to differentiate between biologically oxidizable and biologically inert organic matter.

For the purpose of the present invention, the term “**Biochemical Oxygen Demand (BOD)**” refers to amount of oxygen consumed in natural aerobic biological processes.

For the purpose of the present invention, the term “**Carryover**” refers to active or inactive enzyme entrained with the pulp leaving the enzyme treatment stage.

For the purpose of the present invention, the term “**Consistency**” refers to mass or weight percentage of oven dry fiber in a pulp solution, e.g., pulp and water, or stock (pulp and additives) and water. It is expressed as a percentage of this material in the solution, in terms of bone dry (BD), oven dry (OD), or air dry (AD) weight. Consistency is often described qualitatively as low, medium, or high without reference to a standard nomenclature. The following ranges are

given as a general guide: very low consistency (0 – 1%), low consistency (1 – 8%), medium consistency (8 – 16%), and high consistency (16 – 40%).

For the purpose of the present invention, the term “**retention time**” refers to contact period of pulp with a bleaching chemical; usually measured from the point of chemical addition to the point where residual chemical is washed out or displaced by another chemical.

For the purpose of the present invention, the term “**Medium-Consistency Centrifugal Pump a.k.a (MC) Pump**” refers to a pump which generates localized shear forces high enough to fluidize pulp suspensions up to 15% consistency so that they behave like Newtonian fluids. Air separation and evacuation is an important aspect of pump design, since air would otherwise accumulate in the eye of the pump.

For the purpose of the present invention, the term “**Decker or Gravity Thickener**” refers to a device for increasing the consistency of dilute fiber suspensions up to the 2-8 percent level, consisting of a rotating screen drum which is wholly or partially submerged in an open vat containing the fiber suspension. Water flows into the cylinder by virtue of the difference in liquid level between the vat and cylinder. In one type of design (commonly called a “slusher” or “slush thickener”), the stock moves from the inlet side of the vat through the dewatering zone to the other side of the vat where the stock is discharged. In another design (sometimes call a “roll-type thickener”), pulp is retained on the cylinder and is couched off by a rubber roll.

For the purpose of the present invention, the term “**High Density Storage or Buffer Storage**” refers to large-volume, high-density storage of unbleached or bleached pulp to provide surge capacity between the pulp and paper mills or between sections of the pulp mill, and thus allow for interruptions in either supply or demand. It is also defined as storage of pulp within the 8 to 15% range of consistency.

Description of the invention

One aspect of this invention relates to prebleach treatment of pulp with xylanase enzyme prior to chemical bleaching. The unbleached pulp is treated with luminase xylanase in an amount effective up to an amount of about 10-50g of luminase xylanase per ton of unbleached pulp to enhance subsequent bleaching of the unbleached pulp. The treatment of unbleached pulp is carried out while buffering the unbleached pulp and xylanase enzyme with carbon dioxide to a pH of from about 6.5 to about 7.5 and with a good mixing between pulp and luminase enzyme.

In the preferred embodiment of this invention, the prebleach treatment of pulp with lower levels (e.g., 10-20 g/t) of luminase (a bacterial-produced endo- β -1,4-xylanase) enzymes (e.g., Verenium's Luminase PB-100 and PB-200) to enhance subsequent bleaching of pulp by chlorine dioxide, thus reducing usage of chlorine dioxide. The optimum pH range for prebleaching treatment of pulp with luminase is about 6.8-7.2 (i.e., slightly acidic to slightly neutral) by using acid and preferably carbon dioxide as the pH buffering agent to provide this pH range. A medium consistency (MC) centrifugal pump is required to provide a good mixing of pulp and luminase enzyme. Use of lower levels of luminase enzyme decreases the filtrate chemical oxygen demand (COD) on the pulp bleaching system. In the preferred embodiment of this invention, the luminase enzyme can be added to brownstock or post O2 washer repulper or standpipe prior to medium consistency pump (aka, MC pump). Luminase enzyme is most typically added at the suction side of MC pump following the addition of acid or D filtrate for pH control. Alternatively, the Luminase enzyme can be added at the thick stock pump to improve pulp consistency from 10% to 7% consistency. The enzyme treatment is completed in a brownstock High Density (HD) tower or storage tank.

one further aspect of the present invention is directed to a process that ensures all enzymes are effectively consumed in the enzymatic treatment of the pulp and/or there is no or substantially no active enzymes present in the pulp composition prior to bleaching of the enzyme-treated pulp. The enzyme-treated pulp composition prior to bleaching may contain from 0 to 50g of active xylanase, preferably from 0 to 40g, more preferably 0 to 30 wt%, and most preferably 0 to 20g of active xylanase per ton of enzyme treated pulp. This range may include less than 0.25, 0.5, 1, 2, 3, 4, 5, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, and 50g of active xylanase per ton of pulp transferred to the bleaching step, including any and all ranges and subranges contained therein.

The inventors identified several factors affecting bleach filtrate COD increase in enzyme treatment. The key factors are listed and discussed below:

1- Type of Enzyme – While many xylanase products are available on the market, all xylanase enzymes do not have the same effectiveness in terms of bleaching chemical reduction and the extent of the side effects such as filtrate COD increase. The inventors discovered, Verenium's Luminase xylanase enzyme outperforms other market xylanase products because of the two key differences between Luminase and market xylanase products: 1) Luminase is produced from bacteria rather than fungi for other market xylanase, and 2) Luminase seems to have better penetration and reactivity than other xylanase products (determined collectively by the enzyme's protein size, shape, and charge). The selection of luminase enzyme has made it possible to reduce enzyme dosage that not only improves the net bleaching cost reduction, but provides a mechanism to minimize filtrate COD increase commonly observed in enzyme trials. Traditionally, paper mills used 75-300 g/t enzyme dosage based largely on recommendations

from enzyme suppliers. Dropping the enzyme dosage to 10-50 g/t will substantially reduces the net bleaching cost as well as pulp yield loss and bleach filtrate COD increase

2- Enzyme dosage - There exist an optimum enzyme dosage which above that level, filtrate BOD/COD will increase without improving bleaching cost reduction (actually decreasing net cost savings because of higher enzyme cost). The filtrate COD increase with increasing enzyme dosage. That optimum enzyme dosage was found to be as low as 10 g/t of pulp. Some paper mills applied as high as 300 g/t enzyme dosage in the past. This is believed to be the key reason for the elevated filtrate COD increase associated with xylanase enzyme pulp treatment.

3- Enzyme Conditions – It was noted that pH is perhaps the most important operating parameter in enzyme treatment of pulp. The natural xylanase optimum pH is about 6.5-7.5. If paper mills operate outside of the enzyme optimum pH range, it will reduce the enzyme effectiveness while still increasing filtrate COD. Generally, paper mills add H₂SO₄ to adjust unbleached pulp pH to achieve the optimum enzyme treatment pH in the brownstock HD tower. The inventors discovered that compared with H₂SO₄, CO₂ provides a buffer at a neutral to slightly acidic pH range and improves pH uniformity in the brownstock HD tower. Both effects can translate to more enzyme effectiveness and a lower enzyme dosage. Other key enzyme treatment conditions affecting the effectiveness and COD increase are temperature, retention time, and unbleached pulp carryover.

The temperatures employed in the enzyme treatment stage may vary widely and any temperatures employed in conventional enzyme treatment may be used. For example, useful temperatures can be as low as about 40 °C or lower and as high as about 70 °C or higher. In the

enzyme treatment of this invention, the temperature is usually from about 40 °C to about 70 °C, preferably from about 45 °C to about 65 °C, and most preferably from about 50 °C to about 60 °C.

The retention time employed in the enzyme treatment stage may vary widely and any retention time employed in conventional enzyme treatment may be used. Usually, retention time will be at least about 30 minutes. Retention times are preferably from about 15 min. to about 240 min., and are more preferably from about 30 minutes to about 240 min. and most preferably from about 40 min. to about 240 min.

The consistency (CSC) of the pulp may vary widely and any consistency that provides the desired increase in pulp brightness may be used. The pulp may be treated under low or medium consistency conditions (i.e. from about 2% to about 15% based on the total weight of the mixture of pulp and bleaching chemicals). The consistency is preferably from about 5% to 15%, more preferably from about 8% to 15%, and most preferably from about 10% to about 12%.

Optionally, a washer is disposed after the enzyme treatment step and prior to bleaching to wash the pulp. The washed pulp is then sent to bleaching and the remaining composition may be utilized elsewhere in the process of the invention. For example and preferably in this embodiment, the remaining composition may contain enzyme, preferably active enzyme. Thus, washing the pulp after the enzyme treatment step removes a substantial portion of the enzyme from the pulp composition after the enzyme treatment step and prior to bleaching. When the remaining composition contains enzyme after washing, the composition may in part or in whole be recycled for use at any one or more of the aforementioned upstream enzyme addition points described above in the process of the invention including but not limited to the high shower side or the repulper side of the brown stock decker. Alternatively, the remaining composition containing enzyme after washing may be used as a substitute to dilution water that may be mixed

with fresh Luminase before entered on the repulper side of the brown stock decker. A person of ordinary skill in the art would appreciate that the remaining composition containing enzyme after washing can be added anywhere between the repulper side of the brown stock decker and/or prior to the enzyme treatment step including but not limited to those enzyme addition points described hereinabove in the process of the invention.

4- ClO₂ Usage in D₀ stage- After enzyme treatment, the pulp is much easier to delignify. It is important to reduce the ClO₂ charge in the D₀ stage. If the paper mill operates the D₀ stage at above a critical ClO₂ charge, there is no net improvement in D₀Eop delignification efficiency, while proportionally increasing D₀ stage filtrate COD.

5- pH and Temperature of Eop stage - Lower Eop stage pH is the key to leverage the bleach filtrate COD. Backing off Eop pH is made possible by effective enzyme treatment particularly with using CO₂ for pH adjustment (better enzyme penetration and efficiency due to more buffered pH with CO₂). The reduced Eop pH and temperature also contributes to an improved bleaching cost reduction and a minimum filtrate COD increase. The reduction in the Eop conditions (pH or NaOH charge, temperature and sometime H₂O₂ charge) after enzyme treatment is made possible by the functionality of the luminase enzyme to break down the lignin-xylan bonds, making residual lignin more accessible and reactive for removal in the first two delignification (D₀Eop) stages of the bleach plant. The reduced temperature in the Eop filtrate can improve COD removal efficiency in mill wastewater treatment plant (WWTP).

Subsequently, all the enzyme application principles were applied at one paper mill and have achieved surprisingly excellent results that were not known previously such as:

1) Enzyme pretreatment has allowed the mill to cut all the steam usage off in all of its bleach stages, leading to lower wastewater temperature and improved WWTP operation efficiency.

- 2) The COD increase is minimized to less than 10% with the help of prebleach washer and by manipulating the enzyme dosage and enzyme application (e.g., CO₂) and optimizing D₀Eop delignification operation conditions (e.g., D₀ ClO₂ charge and Eop pH and temperature).
- 3) The actual final effluent COD discharge to one paper mill receiving water after Wastewater Treatment Plant (WWTP) is actually 4% lower with enzyme compared with the period without enzyme because of a) the positive impact of lower wastewater temperature on WWTP operation and b) the readily biodegradable COD (sugars) added from enzyme treatment.
- 4) Specifically, enzyme pretreatment at one paper mill enables the reduction of Eop pH by 0.29 and 0.23 units for SoftWood (SW) and HardWood (HW) respectively. The total temperature reduction in D₀, Eop, and D₁ stages for SW and HW are 8 °C and 6 °C, respectively. There is no impact on paper machine (PM) sizing chemistry.

One paper mill achieved better reduction in bleach chemical and steam consumption and lower additional load of COD from bleach plant compared with other paper mills, attributable to many factors including:

- The use of better xylanase enzyme (Luminase)
- The availability of a pre bleach plant washer to recycle
- The CO₂ use in post O₂ washer
- Availability of a MC centrifugal pump for efficient mixing
- Tight control of enzyme treatment conditions on particularly pH (6.7-7.0)
- Lower enzyme dosage (11-13 g/t versus as high as 500 g/t for other mills)
- Reduction of D₀ kappa factor or ClO₂ charge
- Reduction of D₀ and Eop stage temperature
- Reduction of Eop stage pH.

Since a majority of COD is generated during enzyme treatment prior to ECF bleaching, the prebleach plant washer allows the paper mill to send some part of COD to the recovery boiler for burning rather than sewerage. This has contributed to the observed low COD increase in mill wastewater and is one of the key recommendations for practicing enzyme treatment with minimum COD increase.

For some mills, the aeration power (to increase the dissolved oxygen (DO) level) and macronutrients nitrogen and phosphorus (N and P) concentrations in the wastewater treatment plant needs to be increased to successfully treat a higher COD enzyme treated effluent and for a higher treatment efficiency.

However, one of the advantages of a preferred embodiment of this invention is the reduction of bleaching chemicals such as ClO_2 , H_2O_2 , NaOH , or combination thereof in the Eop and/ or Ep stages as compared to the same or substantially the same bleaching processes which do not include the enzyme treatment stage. For example, the reduction in the amount of H_2O_2 is typically at least about 5 %. In the most preferred embodiments of the invention when hydrogen peroxide is used as a bleaching agent in the Eop or Ep extraction stage. The amount of hydrogen peroxide in the bleaching liquor is preferably from about 5 to about 100 pounds per ton of pulp on a dry basis. The hydrogen peroxide is conventionally obtained from suppliers as a mixture of 50 % water and 50 % hydrogen peroxide on a weight basis, but other proportions of water and hydrogen peroxide can be used, provided they are equivalent to from 5 to 100 pounds of H_2O_2 chemical. These amounts of hydrogen peroxide can be applied to the methods of brightening mechanical as well as chemical pulps according to the present invention. The amount of extraction agent oxidant used (e.g. hydrogen peroxide and hypochlorite) used in the practice of the process of this invention can vary widely and any amount sufficient to provide the desired degree of brightness

can be used. The amount of bleaching agent used is usually at least about 0.2 % based on the dry weight of the pulp. Preferably the amount of bleaching agent is from about 0.5 % to about 1 %, more preferably from about 0.5 % to about 0.8 % and most preferably about 0.5-0.8 % on the aforementioned basis.

In addition, the Eop or Ep pulp brightness and viscosity were higher than those treatments without enzyme treatment, which indicates the positive impact of enzyme treatment on the peroxide efficiency and selectivity in the Ep stage. For example, the viscosity is typically at least about 5 %, preferably at least about 10 %, more preferably from about 5 % to about 15 % and most preferably from about 5 % to about 10 % greater than the viscosity of the pulp made by the same or substantially the same bleaching processes which do not include the enzyme treatment stage. For example, the brightness is typically at least about 2 %, preferably at least about 10 %, more preferably from about 5 % to about 15 % and most preferably from about 7 % to about 10 % greater than the brightness of the pulp made by the same or substantially the same bleaching processes which do not include the enzyme treatment stage.

Conventional process parameters employed in these oxidative extraction stage can be described in, for example “Pulp Bleaching Principles and Practice of Pulp Bleaching” Carlton W. Dence and Douglas W. Reeve, TAPPI Press, 1996 and references cited therein. Accordingly, they will not be described in greater detail.

In the preferred embodiment of this invention in which a prior D₀ extraction stage is used, the pH in the D₀ stage of the present invention is higher than the pH of the conventional D₀ bleaching stage. The advantages of higher pH are higher brightness, less AOX formation, elimination of H₂SO₄ addition and associated BaSO₄ scale formation or a combination of two or more thereof. The pH of the D₀ stage is preferably in the range from greater than 3 to about 6. Any

pH within this range can be used. For example, the pH can be as high as about 4, 5, or 6 and as low as about 2.5 to about 3. In the preferred embodiments of the invention, the pH is from about 3 to about 6. In the more preferred embodiments of the invention, the pH is from about 4 to about 6 and in the most preferred embodiments of the invention, the pH is from about 4.5 to about 5.5.

However, one of the advantages of a preferred embodiment of this invention is the reduction of bleaching chemicals such as ClO_2 in the D_0 stage as compared to the same or substantially the same bleaching processes which do not include the enzyme treatment stage. For example, the reduction in the amount of ClO_2 is typically at least about 5 %, preferably at least about 10 %, more preferably from about 5 % to about 20 % and most preferably from about 10 % to about 20 % less than the amount of ClO_2 used in the same or substantially the same bleaching processes which do not include the enzyme treatment stage to obtain the same or substantially level of pulp brightness in the Eop and or Ep stages. The amount of extraction agent used (e.g. sodium hydroxide, magnesium hydroxide, potassium hydroxide, ect.) used in the practice of the process of this invention can vary widely and any amount sufficient to provide the desired lignin extraction efficiency and the desired degree of brightness can be used. The amount of caustic used is usually at least about 0.5 % based on the dry weight of the pulp. Preferably the amount of bleaching agent is from about 1 % to about 8%, more preferably from about 1.5 % to about 3 % and most preferably about 1-2 % on the aforementioned basis.

In the most preferred embodiments of the invention, the amount of chlorine dioxide in the D_0 extraction stage liquor is preferably from about 10 to about 100 pounds per ton of pulp on a dry basis. The chlorine dioxide is conventionally obtained from suppliers as a mixture of 90 % water and 10 % chlorine dioxide on a weight basis, but other proportions of water and chlorine dioxide can be used, provided they are equivalent to from 10 to 100 pounds of ClO_2 chemical.

These amounts of chlorine dioxide can be applied to the methods of brightening mechanical as well as chemical pulps according to the present invention.

The plant source of pulp for use in this invention is not critical and may be any fibrous plant which can be subjected to chemical pulp bleaching. Examples of such fibrous plants are trees, including hardwood fibrous trees such as aspen, eucalyptus, maple, birch, walnut, acacia and softwood fibrous trees such as spruce, pine, cedar, including mixtures thereof. In certain embodiments, at least a portion of the pulp fibers may be provided from non-woody herbaceous plants including, but not limited to, kenaf, hemp, jute, flax, sisal, or abaca although legal restrictions and other considerations may make the utilization of hemp and other fiber sources impractical or impossible. The source of pulp for use in the practice of this invention is preferably hardwood and softwood fibrous trees, more preferably Eucalyptus, Spruce and Aspen and is most preferably Aspen and Spruce.

The pulp used in the process of this invention can be obtained by subjecting the fibrous plant to any chemical pulping process. Following the wood digestion process, pulp is separated from the spent pulping liquor. The spent pulping liquor is then recovered and regenerated for recycling. The pulp is then bleached and purified in a bleach plant operation.

The pulp of this invention can also be used in the manufacture of paper and packaging products such as printing, writing, publication and cover papers and paperboard products. Illustrative of these products and processes for their manufacture are those described in USP Nos. 5,902,454 and 6,464,832.

For example, in the paper or paperboard making process, the bleached pulp of this invention or pulp mixtures comprising the bleached pulp of this invention is formulated into an aqueous paper making stock furnish which also comprises one or more additives which impart or

enhance specific sheet properties or which control other process parameters. Illustrative of such additives is alum which is used to control pH, fix additives onto pulp fibers and improve retention of the pulp fibers on the paper making machine. Other aluminum based chemicals which may be added to furnish are sodium aluminate, poly aluminum silicate sulfate and poly aluminum chloride. Other wet end chemicals which may be included in the paper making stock furnish for conventional purposes are acid and bases, sizing agents, dry-strength resins, wet strength resins, fillers, coloring materials, retention aids, fiber flocculants, defoamers, drainage aids, optical brighteners, pitch control chemicals, slimicides, biocides, specialty chemicals such as corrosion inhibitors, flame proofing and anti-tarnish chemicals, and the like.

The aqueous paper making stock furnish comprising the bleached pulp and the aluminum based compounds is deposited onto the forming wire of a conventional paper making machine to form a wet deposited web of paper or paperboard and the wet deposited web of paper or paperboard is dried to form a dried web of paper or paperboard. Paper making machines and the use of same to make paper are well known in the art and will not be described in any great detail. See for example, Pulp and Paper Chemistry and Handbook for Pulp & Paper Technologies, supra. By way of example, the aqueous paper making stock furnish containing pulp, aluminum based and other optional additives and usually having a consistency of from about 0.3% to about 1% is deposited from the head box of a suitable paper making machine as for example a twin or single wire Fourdrinier machine. The deposited paper making stock furnish is dewatered by vacuum in the forming section. The dewatered furnish is conveyed from the forming section to the press section on specially-constructed felts through a series of roll press nips which removes water and consolidates the wet web of paper and thereafter to the dryer section where the wet web of paper is dried to form the dried web of paper of this invention. After drying, the dried

web of paper may be optionally subjected to several dry end operations such as and various surface treatments such as coating, and sizing and calendering.

The paper manufactured in accordance with this invention can be used for conventional purposes. For example, the paper is useful as printing paper, publication paper, newsprint and the like.

The present invention is described in more detail by referring to the following examples and comparative examples which are intended to more practically illustrate the invention and not to be a limitation thereon.

Example 1

The lab investigation on Hardwood (HW) pulp shows an excellent Luminase enzyme response in that application of Luminase enzyme at a dosage as low as 10 g/t reduces 20% of ClO_2 and NaOH with 1-2% higher extracted pulp brightness as shown in Table 1.

The filtrate COD in the D_0 stage is strictly dependent upon the enzyme application dosage, decreasing with decreasing enzyme dosage. Therefore, one way to manipulate the filtrate COD increase for luminase enzyme treatment is to control the enzyme dosage rate. Luminase enzyme treatment at 10 g/t for birch pulp bleaching actually leads to a 5% decrease in filtrate COD versus about 10% COD increase at the 15 g/t enzyme dosage while achieving the same 20% of ClO_2 and NaOH reduction at both enzyme dosages. The process results and conditions are set forth in the following Table 1.

Table 1

Table 1 - Birch Pulp Luminase Lab Study					
Luminase Treatment Conditions: 8% CSC, pH 5.6 (w/H_2SO_4), 60 °C, 40 min					
PB 100 enzyme, g/t	0 (Control)	10	15	30	100
Brightness, %		47.5	46.5	47.2	48.4
No washing between Luminase and D_0 stage					
Do: 45 min, 10% CSC, vat pH 4, 60 C					
ClO_2 charge, %	1.15	0.9	0.9	0.9	0.9
Brightness, %	73.7	68.8	70.5	70.9	70.5
Filtrate COD, mg/l	1504	1286	1748	2016	2372
Ep: 45 min, 10% CSC, 70 C, 0.45% H_2O_2					
NaOH charge, %	1.0	0.8	0.8	0.8	0.8
Brightness, %	76.6	77.8	78.3	78.1	78.8
P no	1.8	2.6	2.5	2.4	2.4
Filtrate COD, mg/l	1060	1142	1066	1084	1046

Example 2

The lab results on HW pulps are summarized in Table 2. The luminase enzyme dosage study on HW pulp shows that a luminase dosage at 20 g/t works as well as a high enzyme dosage at 100 g/t. Overall, the HW pulp has excellent response to luminase enzyme, resulting in 6 lb/t (20%) ClO₂ reduction and 3 lb/t (25%) NaOH reduction with 1-2% higher final brightness and viscosity. The process results and conditions are set forth in the following Table 2:

Table 2 - HW Pulp Luminase Lab Study				
Luminase: 65 min, 10% CSC, 60 C				
Luminase, g/t	0	20	30	100
Brightness, %		50.9	51.7	52.2
D0: 20 min, 5% CSC, 63 C, 0.5% H₂SO₄				
ClO ₂ , %	1.0	0.8	0.8	0.8
Brightness, %	72.7	75.5	75.9	76.7
Filtrate COD, mg/l	516	685	770	955
Ep: 90 min, 10% CSC, 0.1% H₂O₂				
Temperature, C	72	72	72	72
NaOH, %	0.6	0.45	0.45	0.45
Brightness, %	74.9	78.4	79.1	79.6
P#	2.8	2.7	2.5	2.3
Filtrate COD, mg/l	776	774	746	714
D1: 180 min, 10% CSC, 0.6% ClO₂				
Temperature, C	72	72	60	60
Brightness, %	87.5	88.6	89.5	89.2
Reverted Brightness, %	85.5	87.0	88.0	87.2
Viscosity, cps	17.2	18.7	19.5	19.5
Tappi Dirt, ppm	0	0	0	0
Filtrate COD, mg/l	332	308	267	284

Examples 3 & 4

As shown in Tables 3 and 4 below, the lab investigation shows excellent HW pulp response to Luminase enzyme treatment. Application of Luminase enzyme at a dosage as low as 30 g/t reduces about 20% of ClO₂ and NaOH with higher extracted pulp brightness without increasing bleach filtrate COD. The chemical cost savings is substantial. Furthermore, the bleaching cost reduction is the same for the enzyme dosage as low as 30 g/t and as high as 125 g/t. The process results and conditions are set forth in the following Table 3.

Table 3
Hardwood Batch

Stage	Control	Low Enzyme Dose	Mid Enzyme Dose	High Enzyme Dose
Enzyme #/adt	0	0.063	0.126	0.252
Do % ClO ₂ / #/adt	0.73/ 13.14	0.6/ 10.8	0.6/ 10.8	0.6/ 10.8
COD mg/L	362	434	444	426
Brightness, ISO	68.4	73.0	72.9	71.9
EOP NaOH %/#/adt	0.9/ 16.2	0.7/12.6	0.7/12.6	0.7/12.6
Temperature °C/°F	80/176	68.3/155	60/140	60/140
COD mg/L	1174	1050	784	680
Brightness, ISO	81.4	82.3	79.9	81.5
D1 % ClO ₂ / #/adt	0.5/ 9	0.5/ 9	0.5/ 9	0.5/ 9
COD mg/L	542	503	525	484
Brightness, ISO	86.8	88.2	88.0	87.9

Hardwood Batch

Stage	Control	High Temp E- Low Enzyme	Mid Temp E- Low Enzyme	Low Temp E- Low Enzyme
Enzyme #/adt	0	.063	.063	.063
Do % ClO ₂ / #/adt	0.73/ 13.14	0.6/ 10.8	0.6/ 10.8	0.6/ 10.8
COD mg/L	344	258	258	258
Brightness, ISO	71.6	73.8	73.8	73.8
EOP NaOH %/#/adt	0.9/16.2	0.7/12.6	0.7/12.6	0.7/12.6
Temperature °C/°F	80/176	70/158	65/149	60/140
COD mg/L	1082	935	788	818
Brightness, ISO	82.6	83.6	83.3	82.3
D1 % ClO ₂ / #/adt	0.5/ 9	0.5/ 9	0.5/ 9	0.5/ 9
COD mg/L	620	568	572	580
Brightness, ISO	89.2	89.1	89.6	89.1

For EO HW pulp, Luminase enzyme treatment did not result in a significant change in filtrate COD. A decrease in Eop temperature however leads to a reduced Eop filtrate COD without adversely affecting the Eop efficiency.

Example 5

Similarly, the luminase enzyme dosage study on pine pulp shows that there is no performance difference between a luminase dosage at 30 g/t and 100 g/t as shown in Table 5. The luminase enzyme of pine pulp results in 4 lb/t (15%) ClO₂ reduction and 4 lb/t (25%) NaOH reduction with a significantly higher final brightness and viscosity. The process results and conditions are set forth in the following Table 5.

Table 5 - SW Pulp Luminase Lab Study			
Luminase: 65 min, 10% CSC, 60 C			
Luminase, g/t	0	30	100
Brightness, %		43.4	43.1
D0: 60 min, 3.8% CSC, 65 C, 0.8% H₂SO₄			
ClO ₂ , %	1.3	1.1	1.1
Brightness, %	68.0	66.2	66.9
Filtrate COD, mg/l	555	655	785
Ep: 110 min, 10% CSC, 73 C, 0.3% H₂O₂			
NaOH, %	0.9	0.7	0.7
Brightness, %	78.2	78.7	79.3
P#	1.0	1.2	1.1
Filtrate COD, mg/l	1036	996	996
D1: 210 min, 10% CSC, 0.41% ClO₂			
Temperature, C	74	65	65
ClO ₂ , %	0.41	0.41	0.41
Brightness, %	88.3	88.7	89.1
Reverted Brightness, %	86.3	86.5	87.0
Viscosity, cps	18.0	20.0	18.7
Tappi Dirt, ppm	0	0	0
Filtrate COD, mg/l	330	252	246

The observed filtrate COD increase for both HW pulp and pine pulp is decreased by reducing luminase enzyme dosage and can be further minimized by dropping Eop temperature.

Excellent luminase enzyme responses were achieved in lab and mill trial/practice for all the pulps investigated, demonstrating the viability of luminase as a non-capital cost reduction approach for mills provided that the effective luminase enzyme treatment conditions in the brown stock HD can be achieved. The filtrate COD can be minimized by carefully controlling the enzyme dosage, mixing, and pH in the luminase application as well as Eop stage pH and temperature.

Xylanase Application Logistics

Xylanase addition and reaction vessel - As discussed hereinabove, the luminase xylanase can be added to brownstock or post O₂ washer repulper or standpipe prior to MC pump. Luminase xylanase is most typically added at the suction side of MC pump following the addition of acid or D filtrate for pH control. The xylanase treatment is completed in a brownstock high density (HD) tower.

The effective low dosage luminase xylanase practice to achieve improved bleaching cost reduction without a pulp yield loss and filtrate COD increase, it requires the implementation of part or all of the following key application strategies where practical:

- a) Improved pH control to 6.5-7.5, preferably 6.8-7.2 is desirable in brownstock high density (HD) tower
- b) Low unbleached pulp COD or saltcake carryover at <10 kg/ton of pulp, preferably <5 kg/t desirable after the washer
- c) Optional use of a pre-bleach plant washer (pre-washer) to reduce carryover and recycle xylanase

d) Reduction in the extraction (E, Eo, or Eop) stage pH by up to 2 units (to as low as 9) and temperature by up to 20 °C (to as low as 60 °C) as compared with the case without luminase xylanase treatment

In the preferred embodiment of this invention, the luminase xylanase can be added to last brownstock or post O2 washer repulper or standpipe prior to a thick stock pump (aka, TS pump) or a medium consistency pump (aka, MC pump). For the paper mills with a MC pump, luminase xylanase is typically added at the suction side of MC pump. For the paper mills with a TS pump, luminase xylanase must be added at the last brownstock or post O2 washer repulper to get initial xylanase and pulp mixing followed by adding mechanical action in the TS pump. The pulp consistency can be diluted from typically 10-12% to 7-8% to further help xylanase distribution and mixing.

Luminase xylanase may be added to the pulp line following the addition of acid or D filtrate for pH control before being pumped to a brownstock high density (HD) tower or storage tank where the xylanase treatment is completed.

The acids used for pH control include, but not limited to, CO₂, H₂SO₄, HCl. The buffering agent CO₂ can be added at the inlet (vat) of the washer to reduce the pH of the pulp while simultaneously reducing pulp carryover. Alternatively, CO₂ can be added at the outlet (repulper) of the washer for pH control.

The addition of a pre-washer will help to practice low-dosage luminase xylanase in three ways: 1) to reduce the unbleached pulp carryover for improved xylanase efficiency (as xylanase preferentially reacts with COD or saltcake carryover in filtrate before reacting with pulp), 2) to recycle residual xylanase, and 3) to allow the pulp mill to send some part of COD to the recovery boiler for burning rather than dumping in a sewer.

Optionally, a washer is disposed after the enzyme treatment step and prior to bleaching to wash the pulp. The washed pulp is then sent to bleaching and the remaining composition may be utilized elsewhere in the process of the invention. For example and preferably in this embodiment, the remaining composition may contain enzyme, preferably active enzyme. Thus, washing the pulp after the enzyme treatment step removes a substantial portion of the enzyme from the pulp composition after the enzyme treatment step and prior to bleaching. When the remaining composition contains enzyme after washing, the composition may in part or in whole be recycled for use at any one or more of the aforementioned upstream enzyme addition points described above in the process of the invention including but not limited to the high shower side or the repulper side of the brown stock decker. Alternatively, the remaining composition containing enzyme after washing may be used as a substitute to dilution water that may be mixed with fresh Luminase before entered on the repulper side of the brown stock decker. A person of ordinary skill in the art would appreciate that the remaining composition containing enzyme after washing can be added anywhere between the repulper side of the brown stock decker and/or prior to the enzyme treatment step including but not limited to those enzyme addition points described hereinabove in the process of the invention.

As noted above, one aspect of the present invention is directed to a process that ensures all enzymes are effectively consumed in the enzymatic treatment of the pulp and/or there are no or substantially no active enzymes present in the pulp composition prior to bleaching of the enzyme-treated pulp. The enzyme-treated pulp composition prior to bleaching may contain from 0 to 50g of active xylanase, preferably from 0 to 40g, more preferably 0 to 30 wt%, and most preferably 0 to 20g of active xylanase per ton of enzyme treated pulp. This range may include less than 0.25, 0.5, 1, 2, 3, 4, 5, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26,

27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, and 50g of active xylanase per ton of pulp transferred to the bleaching step, including any and all ranges and subranges contained therein.

For some mills, because of unusual pulp response to xylanase treatment and/or practical challenges to implement all the application aspects for COD minimization, there still will be some COD increase in bleach filtrate or wastewater to treatment plant during the low-dosage xylanase practice. The mill may increase the aeration power to raise the dissolved oxygen (DO) level to >1 mg/l, preferably to >2 mg/l, throughout the aeration basin and to increase macronutrients nitrogen and phosphorus (N and P) addition to the wastewater to successfully treat a higher COD xylanase treated effluent and for a higher treatment efficiency in wastewater treatment plant. For example, for 100 parts of BOD (COD), about 5 parts nitrogen and 1 part phosphorus is required.

Xylanase application system – The process of making pulp in a pulp bleaching system comprises at least one Do stage and at least one Eop bleaching stage. A prebleach treatment stage comprises pulp and xylanase in an amount of less than 50g of xylanase per ton of pulp. A buffering agent is used for buffering the pulp and xylanase in order to provide a pH in the prebleach treatment stage from about 6.5 to about 7.5.

Brightness

Approximately 5 grams of pulp is rolled or pressed on a disc and is permitted to completely dry. The brightness is measured on both sides of the brightness pad, at least four readings per side and then the average is calculated. These readings are performed on a GE

brightness meter which reads a directional brightness or on an ISO brightness meter which reads a diffused brightness. Both instruments are made by Technidyne Corp.

Viscosity

The viscosity is a measurement used to compare a relative strength property of the pulp. This property is used to determine the percentage of hardwood/softwood for making different grades of paper. A Cannon-Fenske (200) viscometer tube, calibrated for 25 C, is used for testing bleached pulps. The sample size is 0.2000 grams, using 20 ml, 1.0 molar CED and 20ml DI water mixed thoroughly to break down the pulp fiber.

Permanganate Number

The Permanganate Number indicates the amount of lignin that is in the pulp. (The Kappa number is generally used only on the brownstock, while the value for the Permanganate Number is comparative to the bleached pulp.) The procedure for determining the Permanganate Number is:

1. Weigh exactly 1.00 gram sample.
2. Put the sample in a blender with 700 ml DI water and blend about 45 seconds, pour the sample into a battery jar on a stir plate.
3. Add exactly 25 ml of 0.1 N Potassium Permanganate and 25 ml 4N H₂SO₄, starting a timer set for 5 min.
4. When the timer stops, add 6 ml 1 Molar KI and allow it to mix thoroughly to kill the reaction.
5. Titrate to a starch end point with 0.1N Sodium Thiosulfate. Record mls titrated.

6. In 700ml DI water without the pulp sample, use the same reagents and titrate to use as a blank. Using an accurately prepared Potassium Permanganate, the blank should be 25.0
7. Subtract the mls titrated with the sample from the mls titrated for the blank and the result will be the P Number.

Dirt

Pulp dirt count is done by a visual count of all the dirt spots on the brightness pad and is the size weighted sum of the total dirt spots according to a Tappi temperature rate.

Various modifications and variations may be devised given the above-described embodiments of the invention. It is intended that all embodiments and modifications and variations thereof be included within the scope of the invention as it is defined in the following claims.

What is claimed is:

1. A process of making pulp comprising:

treating a pulp with xylanase in an amount of less than 50g of xylanase per ton of pulp, wherein the treating step is carried while buffering the pulp and xylanase with a buffering agent to a pH of from about 6.5 to about 7.5 prior to at least one bleaching stage to form a treated pulp.
2. The process of claim 1 wherein the pulp is unbleached.
3. The process of claim 1 wherein the xylanase is luminase enzyme.
4. The process of claim 1 wherein the luminase is endo- β -1, 4-xylanase.
5. The process of claim 1 wherein the pulp is treated with the xylanase in an amount from about 10g to about 50g per ton of pulp.
6. The process of claim 3 wherein the pulp is treated with the xylanase in an amount from about 30g to about 50g per ton of pulp.
7. The process of claim 1 wherein the buffering agent is selected from a group of carbon dioxide (CO₂) and H₂SO₄.
8. The process of claim 1 wherein the pulp is subjected to a first bleaching stage (D_o) after the treating step.
9. The process of claim 8 wherein the treated pulp causes 10 to 30% reduction of bleaching chemicals in first bleaching stage (D_o) without causing an increase in pulp yield loss and bleached filtrate Chemical Oxygen Demand (COD) loading as compared with a pulp not being treated in accordance to claim 1.

10. The process of claim 8 wherein the treated pulp after the first bleaching stage step (D_o) is subjected to an Eop bleaching stage.
11. The process of claim 10 wherein the treated pulp permits a reduction of pH by 2 units in the subsequent Eop bleaching stage to minimize the filtrate Chemical Oxygen Demand (COD) filtration as compared with a pulp not being treated in accordance to claim 1.
12. The process of claim 11 wherein the pH of treated pulp in Eop bleaching stage is from about 9 to about 11.
13. The process of claim 10 wherein the treated pulp permits a reduction of temperature by 15°C in the Eop bleaching stage as compared with a pulp not being treated in accordance to claim 1.
14. The process of claim 13 wherein the temperature in the Eop bleaching stage is from about 55°C to about 85°C.
15. The process of claim 1 wherein the xylanase is added to the pulp at and/or after the pulp is washed.
16. The process of claim 1 wherein the buffering agent is added to the pulp simultaneously with, prior to, or after the xylanase is added to the pulp.
17. The process of claim 1 wherein the retention time for the treating step of the pulp is from about 15 min. to about 240 min.
18. The process of claim 1 wherein the temperature for the treating step of the pulp is from about 40 °C to about 70 °C.
19. The process of claim 1 wherein the consistency for the treating step is from about 2 % to about 15 %.

20. The process of claim 1 wherein the treated pulp ISO brightness is at least about 2 to 5 % greater than the brightness of the pulp made by the same or substantially the same bleaching processes without the pulp being treated in accordance to claim 1.

21. The process of claim 1 wherein treating the pulp with xylanase in an amount from 10g to of 50g of xylanase per ton of pulp and wherein the treating step is carried while buffering the pulp and xylanase with a buffering agent to a pH of from about 6.5 to about 7.5 prior to at least one bleaching stage.

22. The process of claim 21 wherein treating the pulp with xylanase in an amount from 10g to of 15g of xylanase per ton of pulp and wherein the treating step is carried while buffering the pulp and xylanase with a buffering agent to a pH of from about 6.8 to about 7.2 prior to at least one bleaching stage.

23. The process of claim 1 further comprising a step of recycling unused enzyme from a prewasher and added to an outlet of a washer for pH control.

24. In a pulp bleaching system comprising at least one Do stage and at least one Eop bleaching stage, a prebleach treatment stage which comprises:

pulp;

xylanase in an amount of less than 50g of xylanase per ton of pulp; and

a buffering agent being used buffering the pulp and xylanase to provide a pH in the prebleach treatment stage from about 6.5 to about 7.5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/056487

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C5/00
ADD.

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)
D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/13574 A1 (BIOTECH INTERNATIONAL LTD [AU]; DUNLOP ROBERT WILLIAM [AU]; WANG BIN []) 9 May 1996 (1996-05-09) claims 1-21; examples 10,11 -----	1,2,8, 15,16
X	US 5 834 301 A (JEFFRIES THOMAS W [US] ET AL) 10 November 1998 (1998-11-10) claims 1-12 -----	1
X	US 6 667 170 B1 (MANTYLA ARJA [FI] ET AL) 23 December 2003 (2003-12-23) paragraphs [0141], [0122]; claim 1; example 19 ----- -/--	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

29 November 2011

Date of mailing of the international search report

08/12/2011

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Karlsson, Lennart

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/056487

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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