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(54) FREENESS OF PAPER PRODUCTS

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(57) ABSTRACT

The present invention provides for the optimisation of conditions for treating pulp with a catalyst and hydrogen peroxide to produce a Freeness value (SR) in a web produced from the treated pulp such that the energy required in mechanical agitation of the pulp is reduced.

FREENESS OF PAPER PRODUCTS

FIELD OF INVENTION

[0001] The present invention relates to a new refining process for paper pulp.

BACKGROUND OF THE INVENTION

[0002] Pulp for making paper, tissues, board or related products may be obtained from cellulose from wood and other sources (e.g., hemp, straw, cotton). The vast majority of the raw material is wood pulp, which can be either softwood or hardwood raw material. Softwood fibres come from needle-bearing conifer trees such as pine, spruce, alpine fir, Douglas fir. Hardwood fibres are derived from deciduous trees of various types, such as birch, eucalyptus, and acacia. Mechanical pulp contains most of the original lignin, whilst in chemical pulp most of the lignin has been removed.

[0003] Among the distinguishing differences between softwood (SW) and hardwood (HW) fibres are the length of the individual cellulosic fibres of the wood, the coarseness of the fibres and the stiffness/collapsibility of the fibres.

[0004] Hardwood and softwood must be subjected to specific mechanical treatments (refining) for converting the wood into a fibrous slurry employed in the formation of a paper web. The fibres of cellulose pulp suspensions are mechanically treated to change the fibres' properties. The cellulose pulp suspension is processed into a product having increased tensile/tear strength properties, increased freeness (Shopper-Riegler) values, increased fines, and improved paper/tissue making properties over that of the initial cellulose pulp suspension. Increased freeness values lead to decreased dewatering capabilities for paper/tissue making, which increases the energy required to dry the paper and it will slow down the speed of paper making. On the other hand, too low freeness yields paper/tissues that are not strong enough. Refining is of importance to the properties of both chemical and mechanical pulp. Apart from the dewatering, it should also be noted that the energy consumption during the refining process is high.

[0005] A chemical process to modulate the cellulosic fibres by treatment of fibres by iron salts and hydrogen peroxide has been disclosed in WO 2005/028744; treatment of Kraft softwood pulp leads to fibre properties reminiscent to hardwood fibres.

[0006] WO 2004/022842 discloses a reduced energy process for refining mechanical pulp after treatment with a pectinase enzyme to produce pulp with certain freeness properties.

[0007] EP 0458397 discloses the use manganese 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me_3-TACN) complexes as bleaching and oxidation catalysts and use for textile and pulp bleaching processes.

[0008] United States Application 2001/0025695A1, Patt et al, discloses the use of ClO_4^- and PF_6^- salts of manganese complexes of 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me_4-DTNE) and Me_3-TACN respectively for wood-pulp delignification and bleaching. Whilst a loss of viscosity reported when using a manganese compound comprising Me_4-DTNE is absent or small, the viscosity loss when using a manganese compound comprising Me_3-TACN is much greater, It is known that cellulose having a lower viscosity gives a paper of reduced strength (Pulp Bleaching, Principle and Practice, C. W. Dence, D. W. Reeve ed., Tappi, Atlanta, 1996).

[0009] WO 2007/125517 discloses the use of 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me_4-DTNE) and Me_3-TACN with buffer and sequestrants for bleaching of cellulosic substrates.

[0010] WO 2008/086937 discloses the use of 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me_4-DTNE) and Me_3-TACN for bleaching of cellulosic substrates whilst keeping the pH constant.

[0011] US 2002/0066542 A1 describes transition metal complex compounds of polydentate ligands, in particular of cobalt, and the use of such compounds in a delignifying and bleaching method. Reference experiments conducted with a manganese complex comprising Me_3-TACN showed a market loss in viscosity, whilst the other compounds described did not show significant changes in viscosity.

[0012] It would be desirable to provide a method that permits a paper/tissue producer to use a refining process with a lower level of freeness that yields the same pulp strength properties as conventionally provided by mechanical means.

SUMMARY OF THE INVENTION

[0013] We have found that treating cellulosic fibers using a preformed transition metal complex of azacyclic molecules and hydrogen peroxide, improves the effect of refining of these fibers. Treatment can be either done before, during or after the refining process, typically before or during the refining process. The improved refining properties can be observed by increased tensile strength properties at the same mechanical energy input and same Shopper-Riegler value (SR).

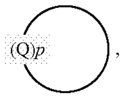
[0014] In addition, despite the facts that within the pulp/paper field it is widely acknowledged that significant reduction of the viscosity loss of cellulose is not desirable for paper-making properties, and that the use of the manganese catalysts comprising Me_3-TACN gives significant viscosity loss, according to different studies, it is particularly surprising to have found that the use of such catalysts leads to an improvement of the effect of refining process on the fiber properties.

[0015] The present invention may be applied to chemical and mechanical pulp, including recycling pulp, for production of paper, tissue or board.

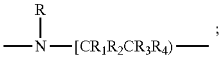
[0016] We have found that energy consumption and time of reaching a cellulose pulp suspension that may be further processed to a web having improved freeness may be reduced by the action of a manganese catalyst together with hydrogen peroxide.

[0017] In a first aspect the present invention provides a method for the treatment of a cellulose pulp suspension comprising (i) the step of subjecting cellulose pulp fibres to an aqueous solution of a manganese transition metal catalyst and hydrogen peroxide at pH from 6 to 13 and (ii) subjecting the pulp to a refining process until a Shopper Riegler (SR) value of from 10 to 90° is reached and the resultant pulp is processed into paper, tissue or board, wherein the manganese transition metal catalyst is present at a concentration from 0.0001 to 1 kg/tonne oven-dry pulp and the hydrogen peroxide is present at a concentration from 0.1 to 100 kg/tonne oven-dry pulp, the manganese transition metal catalyst is preformed and a mononuclear Mn(II), Mn(III), Mn(IV) or dinuclear Mn(II)Mn(II), Mn(II)Mn(III), Mn(III)Mn(III), Mn(III)Mn(IV) or Mn(IV)Mn(IV) transition metal catalyst, the ligand of the transition metal catalyst of formula (I):

(I)



wherein: Q =



$$-N(R)-[CR_1R_2CR_3R_4]-;$$

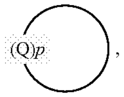
[0018] p is 3;

[0019] R is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl or one of R is linked to the N of another Q from another ring via an ethylene bridge;

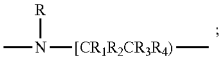
[0020] R1, R2, R3, and R4 are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy.

[0021] In a second aspect, the invention provides the use of an aqueous solution of a manganese transition metal catalyst and hydrogen peroxide at a pH from 6 to 13, wherein the manganese transition metal catalyst is preformed and a mononuclear Mn(II), Mn(III), Mn(IV) or dinuclear Mn(II)Mn(II), Mn(II)Mn(III), Mn(III)Mn(III), Mn(III)Mn(IV) or Mn(IV)Mn(IV) transition metal catalyst, the ligand of the transition metal catalyst of formula (I):

(I)



wherein: Q =



$$-N(R)-[CR_1R_2CR_3R_4]-;$$

[0022] p is 3;

[0023] R is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl or one of R is linked to the N of another Q from another ring via an ethylene bridge;

[0024] R1, R2, R3, and R4 are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy,

[0025] for increasing the extent to which the Freeness Value of cellulose pulp fibres is increased in a refining process.

[0026] According to particular embodiments of the first and second aspect of the invention, each R in the ligand of formula (I) is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl. It is particularly unexpected for these unbridged ligands, wherein no R is linked to the N of another Q from another ring via an ethylene bridge to be suitable for use according to the method of the present invention because of the demonstration in the prior art of the reduction in viscosity found when conducting delignification reactions using transition metal catalysts comprising such a ligand.

[0027] In a further aspect, the invention provides paper, tissue or board obtainable by a method according to the first aspect of the invention or a use according to the second aspect of the invention.

[0028] The Freeness value (SR) is a standard measurement as measured by Shopper Riegler method for Drainability NORM EN ISO 5267-1; the Freeness value (SR) as used herein has been measured by this method.

[0029] The concentration of the catalyst and hydrogen peroxide will have an effect upon the time of refining treatment of the pulp that is required as will the ratio of the mass of pulp to amount of actives used. In this regard, to optimise the conditions the variables of concentration of actives, temperature, pH and time are variables that may be changed.

[0030] It is preferred that the treatment time of the pulp with the catalyst and hydrogen peroxide is from 1 min to 4 h, more preferred 5 min to 3 h, and most preferred 10 min to 2 h. Further, it is preferred that the temperature of the process using the catalyst and hydrogen peroxide is from 30 to 95° C. and more preferably between 40 to 90° C. The pH of the process using the catalyst and hydrogen peroxide is preferably between pH 8 and 12.

[0031] The transition metal complex and hydrogen peroxide may be added at a conventional bleaching stage. Alternatively, the transition metal complex and hydrogen peroxide may be added prior to or during the refining stage, for example to pulp that this already been bleached in one or more delignification and bleaching stages, i.e. to chemical pulp. Chemical pulp thus treated may have been delignified/bleached by contact with hydrogen peroxide and a transition metal catalyst, for example as defined in accordance with the present invention.

[0032] Alternatively, the chemical pulp may be otherwise produced, for example by non-catalytic bleaching of pulp, for example using ozone, chlorine dioxide or non-catalytic bleaching with hydrogen peroxide.

[0033] Alternatively, the manganese catalyst together with hydrogen peroxide may be employed both in a bleaching stage, and again after the bleaching stage, prior to or during the refining stage.

[0034] Often, for mechanical pulp and recycle pulp processing, a bleaching stage, for example involving use of hydrogen peroxide, is conducted. In such cases, the manganese transition metal catalyst defined in accordance with the first and second aspect of the invention could be included as well. Sometimes, a reductive bleaching step with dithionite may be used to treat recycle pulp (to which bleaching step the manganese transition metal catalyst will not be added). Alternatively, the manganese transition metal catalyst and hydrogen peroxide may be used to treat mechanical pulp and recycle pulp, particularly before or during the mechanical refining process, after it has been bleached with hydrogen peroxide and/or with dithionite.

[0035] Alternatively, the manganese catalyst together with hydrogen peroxide may be employed both in a bleaching stage, and again after the bleaching stage, prior to or during the refining stage.

[0036] These possibilities are discussed in greater detail below. A washing step is typically but not necessarily carried out between addition of transition metal catalyst & hydrogen peroxide and the refining process (if the former is effected prior to the latter).

[0037] It will be appreciated that the amount of transition metal catalyst/hydrogen peroxide required per tonne of pulp (oven dry) is essentially that of a molar ratios but within the industry it is normal to express amounts in weight. In this regard, the range of transition metal catalyst required per tonne of pulp (oven dry) is in the range from 0.0001 to 1 kg per tonne of pulp (oven dry) which equates approximately to 0.1 to 1500 mmol/tonne pulp (oven dry). According to particular embodiments of the invention, the transition metal catalyst is present at a concentration in the range from 0.0005 to 0.2 kg per tonne of pulp (oven dry). The hydrogen peroxide (100%) per tonne of pulp (oven dry) is in the range from 0.1 to 100 kg, more preferably 0.5 to 50 kg, most preferably 1 to 30 kg. For example, the hydrogen peroxide (100%) per tonne of pulp (oven dry) may be in the range from 0.1 to 25 kg per tonne of pulp (oven dry). It is to be understood that the each of the ranges of concentration of transition metal catalyst disclosed herein may be combined with each of the ranges of hydrogen peroxide disclosed herein. For example, according to certain embodiments of the invention, the transition metal catalyst is present at a concentration in the range from 0.0005 to 0.2 kg per tonne of pulp (oven dry) and the hydrogen peroxide (100%) per tonne of pulp (oven dry) is in the range from 0.1 to 25 kg.

[0038] The molar ratio of transition metal catalyst:hydrogen peroxide is preferably in the range from 1:100 to 1:10000.

[0039] With the above in mind it is then routine for a technician skilled in the art to determine the conditions by trial and error to produce the Freeness value (SR) and apply the conditions to obtain and optimise the pulp having the desired Freeness value (SR) to a web industrially.

DETAILED DESCRIPTION OF THE INVENTION

[0040] Pulp to produce paper or board grades is fed to a paper machine where it is formed as a paper web and the water is removed from it by pressing and drying. Pressing the sheet removes the water by force. Once the water is forced from the sheet, felt is used to collect the water. When making paper by hand, a blotter sheet is used. Pulp for the manufacturing of tissue or kitchen towel grades is dewatered and dried without pressing, to maintain the appropriate absorbancy and smoothness properties.

[0041] Drying involves using air and or heat to remove water from the paper sheet. In the earliest days of papermaking this was done by hanging the paper sheets like laundry. In more modern times, various forms of heated drying mechanisms are used. On the paper machine, the most common is the steam-heated can dryer. These dryers can heat to temperatures above 200° F. (93° C.) and are used in long sequences of more than 40 cans. The heat produced by these can easily dry the paper to less than 6% moisture.

[0042] Specific procedures exist to produce tissue paper. Reference is made to Paper and Board Grades, Book 18, chapter 4, by the Finnish Paper Engineers' Association and TAPPI (2000).

[0043] We have found that treating a cellulose pulp suspension with a manganese transition metal catalyst and hydrogen peroxide changes the extent to which the pulp reacts to a mechanical refining process, as measured by its freeness value (Shopper-Riegler—SR), to produce a web made from the cellulose pulp suspension. Treatment by the manganese catalyst can be either done before the mechanical refining, during, or after the mechanical refining process. For example, and as is discussed below, the catalyst/hydrogen peroxide may be added to a pulp blend or a pulp stock chest, after mechanical refining, where pulp may be stored prior to dewatering.

[0044] The ratio between tensile strength and freeness is improved, i.e., either an increased strength at the same freeness value or same strength at a lower freeness value. By monitoring the conditions of treatment optimum freeness value of a final product is obtained. Further, increased bulk at the same refining can be achieved, particularly important for tissue paper.

[0045] We have found that treating a cellulose pulp suspension and monitoring the variables of concentration and time permits an optimum freeness value for different periods of time.

[0046] The term oven dry pulp is one where pulp has been dried at 100-105° C. to yield a constant weight. Reference is made to TAPPI-test T240 om-93 (1993).

[0047] Refining

[0048] Different types of equipment are frequently used to mechanically treat the cellulosic pulp. Beaters, including Hollander beaters, have been used in many mills, but have now largely replaced by conical and disk refiners, which can operate in continuous processes. Conical refiners are of the shallow angle refiners (Jordan), medium angle refiners (Conflo) and wide angle refiners (Claflin). The group disk refiners comprises three types, single disc, double disc multi-disc refiners.

[0049] Refining can be done at low consistency (2-6%), medium consistency (10-20%) or high consistency (30-35%). Depending on the requirements of the end product, different choices for optimal consistency processing can be made. Reference is made to Paper and Board Grades, Papermaking Part 1. Stock Preparation and Wet End, Book 18, chapter 4, by the Finnish Paper Engineers' Association and TAPPI (2000).

[0050] Processes can be either batch-wise or in a continuous manner, the latter being often preferred due to cost reasons and easier control of quality.

[0051] In many cases different types of wood pulp are mixed, such as softwood and hardwood pulp. One of those or both may be refined independently. Often, more refiners are employed in series, to enhance the benefits/energy requirements, to treat the pulp.

[0052] Refining may take place for chemical pulp, mechanical pulp and recycle pulp, all objects of the current invention.

[0053] Depending on the application, different levels of refining can be done. For tissue and kitchen towel grades, a low refining is carried out, to ensure a good bulk, softness, absorbancy and brightness. A low refining is beneficial for above properties, but negatively impacts the strength properties. Therefore, often wet- and/or dry-strength agents are added. Shopper-Riegler values of between 10 and 30° are often obtained, after refining.

[0054] For printing and writing paper, printability and machine runnability are key parameters. The paper must be clean and bright, have the appropriate smoothness, compressibility, ink-penetration capabilities and sufficient strength for the printing operations. A minimum opacity is another important feature. Therefore, these papers need good refining control to develop the internal bond strength and to obtain the right level of smoothness and formation for its end use. Bleached board grades, used a.o. for packaging frozen foods and liquids, and for paper plates and cups, need good stiffness and bulk with proper smoothness and printability. Also internal bond, creasability and dimensional stability are important factors. Therefore sufficient refining to get these properties will also be needed (without decreasing the bulk and stiffness too much). Shopper-Riegler values after refining of between 15 and 50° are often needed for these applications.

[0055] Dense papers need significant amount of refining, depending on the particular product needs. Release-base papers, glassine, and greaseproof paper all require extensive refining to get the desired balance of strength and appearance properties. Especially if the objective is to make transparent papers, considerable energy requirements are needed for the refining processes. SR values as high 90° can be needed.

[0056] Mechanical pulp needs often refining to produce the paper or board materials exhibiting the appropriate physical properties. Shopper-Riegler values of between 20 and 80° are often reached when refining mechanical pulp.

[0057] The extent of refining can be monitored on-line. Energy input is the most important parameter to determine the extent of refining. Control systems exist to on-line monitor the refining process and adjust energy input according the requirements. Probes to monitor the refiner load, temperature changes, flow/consistency, drainage/freeness (SR), etc. Main process variables include temperature, pH, consistency, additives, pretreatments, production rate, and applied energy.

[0058] Treatment of Cellulosic Fibers by Manganese Catalyst and Hydrogen Peroxide

[0059] Application of the manganese catalyst and hydrogen peroxide to treat the cellulosic fibers can be done at different stages during the fiber treatment/paper making process. This can be either before the mechanical refining process, during the mechanical refining process or after the mechanical refining process, typically before or during the mechanical refining process.

[0060] Typically pulp that has been bleached in one or more delignification and bleaching stage, chemical pulp, can be used to treat further to produce tissue, paper or board. However, within the scope of this invention, also lignin-containing pulp (mechanical pulp) or recycled wood pulp can be used. For integrated mills a wet pulp slurry is brought into the paper mill. When paper producers obtain pulp from other mills, the pulp sheets are first put into a chest and disintegrated to obtain a diluted pulp slurry, which can be further processed.

[0061] In the pulp mills, chemical pulp is commonly bleached by hydrogen peroxide and/or other bleaching processes using for example ozone or chlorine dioxide. Mechanical and recycle pulp are often bleached with hydrogen peroxide to increase brightness of the pulp. During one or more of these bleaching stages, hydrogen peroxide together with the manganese catalyst can be employed to obtain cellulose that can be treated in the refining process. The manganese catalyst and hydrogen peroxide can be added during different stages in the pulp mill.

[0062] In a pulp mixer, chemicals are added to the pulp, which is then mixed very thoroughly. Within the scope of this invention, catalyst and hydrogen peroxide could be added to the pulp mixer to achieve treatment of the pulp. This can be done in low consistency mixers (continuous stirred mixers, tower mixers, dynamic mixers or static mixers), medium consistency mixers (peg mixers, high shear mixers) or high consistency mixers, including Kneader and disc-type mixers. In a steam mixer, steam is added to the pulp to increase the temperature of the pulp. The catalyst and hydrogen peroxide may also be added to the pulp in the steam mixer.

[0063] Reference is made to Pulp Bleaching, Principle and Practice, C. W. Dence, D. W. Reeve ed., Tappi, Atlanta, 1996, infra).

[0064] After adding the pulp bleaching chemicals in the mixers, the bulk of the pulp bleaching takes place in the pulp bleaching tower, after which the pulp is washed. As bleaching processes are generally slow (2-4 h are typical), the bleaching towers tend to be large. However, also smaller pulp retention pipes are sometimes employed to allow certain bleaching or treatment reactions to occur. As the processes are generally continuous, the pulp is either moving slowly upwards (upflow tower), downwards (downflow tower), or a combination thereof (upflow-downflow tower). Within the scope of this invention, the treatment by the catalyst and hydrogen peroxide, may be much shorter, allowing relatively small treatment towers.

[0065] In a pulp washer usually the pulp treated with chemicals in a previous stage of the treatment process are washed out. For example, acidic chlorine dioxide is washed with NaOH solution, to remove alkaline-soluble lignin residues and make the pulp ready for the next stage. Within the scope this invention, the manganese catalyst and hydrogen peroxide could be added into an (additional) mixer, making use of its fast reaction kinetics to treat the pulp with the catalyst.

[0066] A pulp storage tower is designed to store pulp to process further after a period of time. Usually such storage tower can be found before the processes where the pulp bleaching stages are taken place or after the final bleaching stage, before e.g. transporting to the paper mill. Catalyst and hydrogen peroxide can be added together with the pulp entering this storage tower, allowing a slow treatment process of the pulp.

[0067] A pulper is used to dilute waste paper (deinked pulp) and to add alkaline and hydrogen peroxide for bleaching of deinked pulp. The manganese catalyst could be added in this pulper to allow the treatment of deinked pulp by the catalyst.

[0068] Also the manganese catalyst and hydrogen peroxide can be added to the cellulosic pulp before the refining process in the paper mill, such as in the pulper, high density pulp chest, pulp latency chest, pulp mixing chest or pulp levelling chests. The pulper and high density chest are commonly used to prepare dry raw material, half stuff and recycle paper into a pumpable state by addition of water and then mixing with water. In the pulp mixing chest, two or more different types of pulp, optionally refined, are mixed and stored for further processing, such as softwood and hardwood pulp. In levelling chests the consistency of wood pulp is lowered to desired levels.

[0069] Mechanical pulp is often treated in latency chests to treat the fibers that are distorted (kinked, curled, or twisted). Typically mechanical pulp is diluted to 1-2% consistency, heated to 70-90° C., agitated for at least 20 minutes, after which it is further processed. Pulp stock chests are, similarly to the pulp storage described above, used to store the wood pulp. Also the other above-mentioned chests are often used to store the wood pulp and ensure a constant flow of pulp to be treated in the subsequent processes. The wood pulp may be shipped from pulp bleaching mills or it may have been produced on site (integrated mill).

[0070] Alternatively the catalyst/hydrogen peroxide can be added just before the pulp refiner and be allowed to react with the cellulose during the refining process. Due to heat evolution during refining, the additional energy requirement to obtain an optimal treatment effect by the catalyst will be reduced or absent. Different refining equipment can be used, which includes beaters; Hollander beaters; shallow-angle conical refiners; medium-angle conical refiners; wide-angle conical refiners; single-disc refiners; double-disc refiners; multi-disc refiners. Reference is made to Paper and Board Grades, Papermaking Part 1. Stock Preparation and Wet End, Book 18, chapter 4, by the Finnish Paper Engineers' Association and TAPPI (2000) and C. F. Baker, Tappi Journal, 78, 147, 1995.

[0071] Finally, the catalyst/hydrogen peroxide may be added after the mechanical refining stage, in for example in the pulp blend chest (where the different wood pulp sources are mixed) or pulp stock chest. For example mechanical pulp may be treated this way.

[0072] Alternatively, the manganese catalyst together with hydrogen peroxide may be employed both in a bleaching stage, and again after the bleaching stage, prior to or during the refining stage.

[0073] Transition Metal Catalyst

[0074] The manganese transition metal catalyst used may be non-deliquescent by using counter ions such as PF_6^- or ClO_4^-. However, it is preferred for industrial substrates that the transition metal complex is water soluble. It is preferred that the preformed transition metal is in the form of a salt such that it has a water solubility of at least 30 g/l, for example at least 50 g/l at 20° C. Preferred salts are those of chloride, acetate, sulphate, and nitrate. These salts are described in WO 2006/125517.

[0075] According to particular embodiments of the invention, each R in the ligand of formula (I) is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl. According to particular embodiments, R is independently selected from: hydrogen, CH3, C2H5, CH2CH2OH and CH2COOH.

[0076] Preferably, R1, R2, R3, and R4 are independently selected from: H and Me.

[0077] According to particular embodiments, R, R1, R2, R3, and R4 are independently selected from: H and Me. Most preferably, the catalyst is derived from 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3-TACN).

[0078] The preformed transition metal catalyst salt is preferably a dinuclear Mn(III) or Mn(IV) complex with at least one O^{2-} bridge. According to certain embodiments of the invention, the transition metal catalyst may be a salt, such as the salts described hereinbefore, of the complex $[Mn(IV)_2(\mu\text{-}O)_3(Me_3TACN)_2]^{2+}$.

[0079] The level of application of the manganese catalysts can vary depending on the application, but will be typically between 0.0005 and 0.2 kg/t oven-dry pulp (o.d.p.).

[0080] Hydrogen Peroxide

[0081] The hydrogen peroxide is provided as an aqueous solution per se, or as peroxy salts, such as, percarbonate, etc. However, for cost reasons liquid hydrogen peroxide is preferred. A preferred level of hydrogen peroxide applied is: 0.1 kg/t to 100 kg/t oven dry pulp (o.d.p.), more preferable 0.3 to 50 kg/t o.d.p. and most preferred 0.5 to 25 kg/t o.d.p.

[0082] The reagents are preferably provided in an alkali medium, optimally between pH 8 and 13, the alkalinity of which is preferably provided by sodium hydroxide or sodium carbonate.

[0083] The temperature of the treatment process is preferably between 30° C. and 95° C. and more preferably between 40° C. and 90° C.

[0084] The time of the treatment with the catalyst and hydrogen peroxide is between 1 minute and 4 hours, more preferably between 5 minutes and 3 hours, and most preferably between 10 minutes and 2 hours.

[0085] Sequestrant

[0086] Many sequestrants are suitable for use with the present invention. Examples include aminophosphonate and carboxylate sequestrants, for example aminophosphonate and aminocarboxylate sequestrants. Suitable sequestrants include ethylenediamine tetra-acetate (EDTA), the polyphosphonates such as Dequest™ and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid).

[0087] The sequestrant used in the treatment step with manganese catalyst and hydrogen peroxide is preferably an aminocarboxylate sequestrant or mixtures thereof. The following are preferred examples of aminocarboxylate sequestrants: ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylenediaminetetraacetic acid (HEDTA), iminodisuccinic acid (IDS), nitrilotriacetic acid (NTA), N-hydroxyethylaminodiacetic acid, diethylenetriaminepentaacetic acid (DTPA), methylglycinediacetic acid (MGDA), ethylenediamine di-succinic acid (EDDS) and alanine-N,N-diacetic acid. A most preferred aminocarboxylate sequestrant is diethylenetriaminepentaacetic acid (DTPA).

[0088] Phosphonate sequestrants may also be used; a preferred phosphonate sequestrant is Dequest 2066 (Diethylenetriamine Penta(methylene phosphonic acid sodium salt).

[0089] It will be understood that, where used, a sequestrant may be present in the free acid or salt form. For example, were present in salt form, this may be an alkali metal, alkaline earth metal, ammonium or substituted ammonium salt. Typically, a sequestrant, if present, is in its free acid form or as a sodium, potassium or magnesium salt. An example of a sodium salt of an aminocarboxylate sequestrant is the pentasodium salt of diethylenetriamine penta(methylene phosphonic acid, commercially available under the trade name Dequest 2066A.

[0090] The most preferred concentration of the sequestrant used in the method is 0.01 to 50 kg/ton oven dry pulp in the solution containing the manganese catalyst and hydrogen peroxide, most preferably 0.03 to 20 kg/ton oven dry pulp.

[0091] Experimental

[0092] Experiment 1: Treatment of softwood pulp with hydrogen peroxide with and without $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ at pH 11.0 (Me_3-TACN=1,4,7-Trimethyl-1,4,7-triazacyclononane).

[0093] $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ (as 3.5% aqueous solution) was obtained as disclosed elsewhere (WO2006/125517).

[0094] Softwood pulp with a starting ISO-brightness of 49.9 was treated as follows: To a polyethylene (PE) bottle containing 250 g of oven-dry pulp at 10% consistency, was added 10 kg/odtp H_2O_2 (odtp=oven-dry ton pulp—equals to 29.4 mM H_2O_2) and 7.2 kg/odtp NaOH (equals to 18 mM NaOH). Depending on the experiments 0.04 kg/odtp $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ (equals to 6.5 μM $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$)was added and 1.0 kg/odtp DTPA (Diethylenetriaminepenta-acetic acid, pentasodium salt)—(ex Akzo Nobel; trade name Dissolvine D50; purity is 50%). The initial pH-value was pH 11.0 (measured at 20° C.).

[0095] Note 1: This softwood pulp has been delignified in a O_2-delignification step, and partly further bleached by a ClO_2 step.

[0096] Note 2: In practice, pulp was used that contained 35.6% dry matter and 64.4% water (35.6% dry content). Therefore 702.3 g of 'wet' pulp was used for each experiment.

[0097] Note 3: All experiments were carried out at 10% consistency.

[0098] The PE bottles are put in a pre-heated water bath (62.5° C.) for 1 hour and are shaken throughout the bleaching process. Subsequently the pulp mixture is filtrated through a Buchner funnel and washed with copious amounts of demineralised water. Using the filtrate, the H_2O_2 consumption is measured. The following analyses are carried out on the bleached pulp: kappa number, brightness and intrinsic viscosity.

[0099] The results of the experiments are given in Table 1.

TABLE 1

Results of treatment of softwood pulp using $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$, $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ and DTPA and no $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ at an initial pH 11.0 at 60° C. for 60 minutes.

N°	Sample	Brightness (ISO %)	Intr. Visc. (ml/g)	Kappa #	H_2O_2 consumption (kg/odtp)
U	Untreated (raw)	49.9	764	8.33	
P1	Blank (no catalyst, no DTPA)	67.4	753	4.27	7.5
P2	0.04 kg/odtp $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ and 1 kg/odtp DTPA	68.1	701	4.11	7.8
P3	0.04 kg/odtp $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$	66.8	698	4.17	9.6

[0100] The results gathered in Table 1 show that the addition of $[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ has some effect on the bleaching and kappa value and a clear effect on viscosity (degree of cellulose polymerization) of softwood pulp.

[0101] The treated pulp was desintegrated (DIN EN ISO 5263-1; 2004-12), beaten (PFI-mill) (ÖNORM EN ISO 5264-2; 2003-05) and the drainability (Schopper-Riegler method, ÖNORM EN ISO 5267-1; 2000-10) was tested.

[0102] Laboratory handsheets were prepared by the Rapid-Köthen method (ÖNORM EN ISO 5269-2; 2005-04) and conditioning of the samples, NC 23/50 was carried out (DIN EN 20187; 1993-11). The following tests were conducted using the handsheets: grammage (DIN EN ISO 536; 1996-08), thinkness, bulk and density (DIN EN ISO 534; 2005-05), air permeance (Bendtsen, ISO 5636/3; 1992-09), tensile force, stretch at break, tensile strength, tensile index, TEA and elastic modulus (DIN EN ISO 1924-2; 2009-05), internal bond strength (z-direction, TAPPI 541 om-05; 2005), tearing resistance, tear index (ÖNORM EN 21974; 1994-09).

[0103] The results are given in the following tables.

TABLE 2

Results of beating and drainability of bleached softwood pulp after having been treated according to the conditions given in Table 1.

Sample Drainability	P1 [SR]	P2 [SR]	P3 [SR]
Unbeaten	14.0	13.8	14.0
PFI 2000 Revolutions	15.9	16.2	16.9
PFI 5000 Revolutions	24.1	24.3	23.2
PFI 7000 Revolutions	32.7	32.8	32.9
PFI 9000 Revolutions	41.6	46.5	45.5

P1: no catalyst, no DTPA
P2:$[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ and DTPA
P3$[Mn_2(\mu\text{-}O)_3(Me_3TACN)_2](CH_3COO)_2$ without DTPA

[0104] The results gathered in Table 2 show that the pulp samples treated with the catalyst and hydrogen peroxide exhibit similar SR values till 7000 revolutions as the reference, whilst increase SR values are obtained when the pulp is refined at 9000 revolutions.

TABLE 3

Strength and tear values of handsheets prepared using pulp refined at 5000 revolutions as shown in Table 2.

Sample		P1 5000rev	P2 5000rev	P3 5000rev
Grammage	$[g/m^2]$	80.2	81.0	80.2
Thickness	[μm]	111	112	113
Density	$[g/cm^3]$	0.724	0.725	0.711
Bulk	$[cm^3/g]$	1.380	1.380	1.407
Air permeance (Bendtsen)	[ml/min]	429	435	560
Tensile force	[N]	101	111	108
Stretch at break	[%]	2.96	2.89	2.89
Tensile strength	[kN/m]	6.74	7.42	7.21
Tensile index	[Nm/g]	84.1	91.6	89.9
TEA	$[J/m^2]$	136	144	141
Elastic modulus	[GPa]	6.33	6.92	6.76
Internal bond strength	$[N/cm^2]$	82.6	81.5	84.1
Tearing resistance	[mN]	877	827	814
Tear index	$[mN \cdot m^2/g]$	10.9	10.2	10.2

[0105] The results gathered in Table 3 show that the pulp samples treated with the catalyst and hydrogen peroxide and then refined at 5000 revolutions in the PFI mill, show increased tensile strength, tensile energy absorption (TEA) and tensile index values, decreased tearing resistance and tear index, whilst the other parameters are largely unaffected by the treatment using the catalyst and hydrogen peroxide (all with respect to reference without catalyst—P1). A slight enhanced of these tensile strength properties when the catalyst was employed in combination with DTPA.

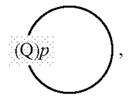
1. A method for the treatment of a cellulose pulp suspension comprising:

(i) subjecting cellulose pulp fibres to an aqueous solution of a preformed manganese transition metal catalyst and hydrogen peroxide at pH from 6 to 13, wherein the manganese transition metal catalyst is present at a concentration from 0.0001 to 1 kg/tonne oven-dry pulp, and the hydrogen peroxide is present at a concentration from 0.1 to 100 kg/tonne oven-dry pulp;

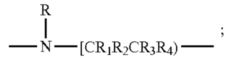
(ii) subjecting the cellulose pulp fibres treated by step (i) to a refining process until a Shopper Riegler (SR) value of from 10 to 90° is reached and the resultant pulp is processed into paper, tissue or board; and

wherein the manganese transition metal catalyst is a mononuclear Mn(II), Mn(III), Mn(IV) or dinuclear Mn(II)Mn(II), Mn(II)Mn(III), Mn(III)Mn(III), Mn(III)Mn(IV) or Mn(IV)Mn(IV) transition metal catalyst, having a ligand of formula (I):

(I)



wherein: Q =



$$-N(R)-[CR_1R_2CR_3R_4)-\ ;$$

p is 3;

R is independently selected from the group consisting of: hydrogen, C_1-C_6-alkyl, CH_2CH_2OH, CH_2COOH, and pyridin-2-ylmethyl; and

R_1, R_2, R_3, and R_4 are independently selected from the group consisting of: H, C_1-C_4-alkyl, and C_1-C_4-alkylhydroxy.

2. The method according to claim **1**, wherein the manganese transition metal catalyst is present at a concentration from 0.0005 to 0.2 kg/tonne oven-dry pulp and the hydrogen peroxide is present at a concentration from 0.1 to 25 kg/tonne oven-dry pulp.

3. The method according to claim **1**, wherein R is independently selected from the group consisting of: hydrogen, CH_3, C_2H_5, CH_2CH_2OH, and CH_2COOH.

4. The method according to claim **1**, wherein R, R_1, R_2, R_3, and R_4 are independently selected from: H and Me.

5. The method according to claim **1**, wherein the catalyst is derived from 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3-TACN).

6. The method according to claim **1**, wherein the pulp is subjected to a refining process until a Shopper Riegler (SR) value of from 10 to 30° is reached, to produce tissue paper.

7. The method according to claim **1**, wherein the pulp is subjected to a refining process until a Shopper Riegler (SR) value of from 15 to 50° is reached, to produce printing and writing paper.

8. The method according to claim **1**, wherein the pulp is subjected to a refining process until a Shopper Riegler (SR) value of from 50 to 90° is reached, to produce tracing and transparent paper.

9. The method according to claim **1**, wherein mechanical pulp is subjected to a refining process until a Shopper Riegler (SR) value of from 20 to 80° is reached.

10. The method according to claim **1**, wherein the catalyst and hydrogen peroxide is added to the cellulose pulp fibres in a device selected from the group consisting of: a pulper, a high density pulp chest, a pulp washer, a pulp latency chest, a pulp levelling chest, a pulp mixing chest, a pulp refiner, a pulp dilution tank, and a pulp stock chest.

11. The method according to claim **10**, wherein the pulp refiner is selected from the group consisting of: beaters, Hollander beaters, shallow-angle conical refiners, medium-angle conical refiners, wide-angle conical refiners, single-disc refiners, double-disc refiners, and multi-disc refiners.

12. The method according to claim **1**, further comprising bleaching the cellulose pulp fibres, wherein the manganese transition metal catalyst and hydrogen peroxide in step (i) is added during the bleaching.

13. The method according to claim **12**, wherein the manganese transition metal catalyst and hydrogen peroxide is added to the cellulose pulp fibres in a device selected from the group consisting of a pulp mixer, a pulp bleaching tower, a pulp retention pipe, a pulp washer, a pulp storage tower, a steam mixer, and a pulper.

14. The method according to claim **1**, wherein the cellulose pulp fibres have been previously subjected to a bleaching stage.

15. The method according to claim **1**, wherein the aqueous solution of step (i) further comprises from 0.01 to 50 kg/ton oven dry pulp of an organic sequestrant selected from: an aminophosphonate sequestrant and a carboxylate sequestrant.

16. The method according to claim **15**, wherein the organic sequestrant is selected from the group consisting of: diethylenetriamine penta(methylene phosphonic acid sodium salt), MGDA (methylglycindiacetate), GLDA (glutamic acid diacetate), IDS (iminodissucinate), EDDS (ethylenediaminedisuccinate), EDTA (ethylenediamine-tetraacetate), and DTPA (diethylenetriamine-pentaacetate).

17. A method according to claim **1**, wherein an energy input into the refining process is monitored and based upon an energy input threshold for cellulose pulp fibres to be processed into paper, tissue, or board.

18. (canceled)

19. (canceled)

20. Paper, tissue or board obtained by a method according to claim **1**.

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