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(57) **Abrégé/Abstract:**

A process of treating a cellulose-lignin pulp. In an ozone stage, the pulp is contacted with ozone to bleach and delignify the pulp. The ozone stage is conducted without the addition of a peroxide bleaching agent. A chelant is introduced into the ozone stage to improve selectivity of the delignification.



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WO 2007/070527 A2

TITLE

PROCESS FOR TREATING A CELLULOSE-LIGNIN PULP

BACKGROUND OF THE INVENTION

[0001] This invention relates in general to processes for treating cellulose-lignin materials and in particular to a process for treating a cellulose-lignin pulp such as a wood pulp.

[0002] Wood contains two main components: a fibrous cellulose portion and a non-fibrous lignin portion. The polymeric chains forming the fibrous cellulose portion are aligned with one another and form strong associated bonds with adjacent chains. The lignin is a three-dimensional polymeric material that bonds the cellulosic fibers and is also distributed within the fibers themselves.

[0003] The wood is converted to pulp for use in paper manufacturing. Pulp comprises wood fibers capable of being slurried or suspended and then deposited on a screen to form a sheet of paper. There are two main types of pulping techniques: mechanical pulping and chemical pulping. In mechanical pulping, the wood is physically separated into individual fibers. In chemical pulping, the wood chips are digested with chemical solutions to solubilize a portion of the lignin and thus permit its removal. The commonly used chemical pulping processes include: (a) the kraft process, (b) the sulfite process, and (c) the soda process. The kraft process is the most commonly used and involves digesting the wood chips in an aqueous solution of sodium hydroxide and sodium sulfide. The wood pulp produced in the pulping process is usually separated into a fibrous mass and washed.

[0004] The wood pulp after the pulping process is dark colored because it contains residual lignin not removed during digestion which has been chemically modified in pulping to form chromophoric groups. In order to lighten the color of the pulp, so as to make it suitable for white paper manufacture, it is necessary to remove the residual lignin by use of delignifying materials and by chemically converting any residual lignin into colorless compounds by bleaching.

[0005] Conventionally, delignification and bleaching of wood pulp has been carried out with elemental chlorine. Although chlorine is a very effective bleaching agent, the effluents from chlorine bleaching processes contain large amounts of chlorides produced as the by-product of these processes. These chlorides readily corrode processing equipment, thus requiring use of costly materials in the construction of bleach plants. In addition, there are concerns about the potential environmental effects of chlorinated organics in effluents.

[0006] To avoid these disadvantages, the paper industry has attempted to reduce or eliminate the use of elemental chlorine for delignification and bleaching of wood pulp. In this connection, efforts have been made to develop a bleaching process in which chlorine-containing agents are replaced, for example, by oxygen for the purpose of bleaching the pulp. The use of oxygen does permit a substantial reduction in the amount of elemental chlorine used. However, the use of oxygen is often not a completely satisfactory solution to the problems encountered with elemental chlorine. Oxygen is not as selective a delignification agent as elemental chlorine, and as a result it not only delignifies the pulp, it also degrades and weakens the cellulosic fibers of the pulp. Also, oxygen delignification usually leaves some remaining lignin in the pulp which must be removed by chlorine bleaching to obtain a fully-bleached pulp, so concerns associated with the use of chlorine still persist.

[0007] Ozone delignification and bleaching of wood pulp is a process that would greatly benefit the industry if it can be arranged to work efficiently. Ozone has a very high oxidation potential, and is thought to have the potential to be a very efficient delignification agent. Ozone potentially could benefit the industry by allowing additional closure of the delignification-bleaching process. Since an ozone stage would not add any detrimental ions to the black liquor recovery stream, its wash effluent could be used counter-currently with prior stages. By this means, fuel to the recovery boiler would be increased, and water-borne pollutants would be decreased. Therefore, the driving force for using ozone is thought to be environmental improvement.

[0008] The deterrents to using ozone have been that ozone has been shown to not meet selectivity requirements, medium consistency stages are not as effective as low or high consistency, and relatively low temperatures are required. Delignification selectivity must be improved if ozone is to be accepted by the paper industry. Current systems do not produce pulp that meets industry pulp strength needs. Limitations using medium consistency and higher temperature can be worked around, but elimination of these constraints will certainly make use of ozone more attractive. Since bleach plants are medium consistency, retrofitting either low or high consistency stages can be problematic. Low temperature for ozone stages is particularly problematic with the closed systems of modern bleach plants.

[0009] Process changes that have been tried to improve ozone bleaching include optimization of pH, consistency, and temperature. The process is improved at lower pH. Low or high consistency is better than medium consistency. Low temperature will improve the process. However none of these process changes have brought the process to meet industry needs.

[0010] Several patents disclose the use of ozone in pulping processes or delignification-bleaching processes. For example, U.S. Patent 6,258,207 by Pan discloses a process aimed at pulping non-woody species. The process consists of three stages: acidic chelation stage; followed by alkaline peroxide stage with chelation, which may or may not be enhanced with either ozone or peracetic acid; followed by a final stage of mechanical pulping. The process is aimed at grasses such as hemp and wheat straw.

[0011] U.S. Patent 5,034,096 by Hammer et al. discloses a process for bleaching and delignifying cellulose containing material using peroxides, oxygen, and/or ozone with the addition of cyanamide or cyanamide salt. When the process includes a peroxide as a bleaching agent, the process also includes a stabilizer or complex former to avoid decomposition of the peroxide. The addition of the stabilizer or complex former can be omitted if the heavy metal salts in the cellulose are removed by washing the cellulose prior to the bleaching.

[0012] U.S. Patent 6,302,997 by Hurter et al. discloses a process that applies only to nonwood species. The process appears to include an acidic chelation ahead of an ozone stage with or without washing in between.

[0013] U.S. Patent 5,593,544 by Fahlgren et al. applies to any comminuted cellulosic fiber. The process consists of sequestering agent treatment prior to an oxygen "digestion" stage. At least some of the chelation filtrate must be removed prior to the oxygen step. The oxygen stage is followed by a hydrogen peroxide bleach that may contain peracetic acid or ozone. No mention is made of using chelation with the peroxide-ozone stage.

SUMMARY OF THE INVENTION

[0014] This invention relates to a process of treating a cellulose-lignin pulp. In an ozone stage, the pulp is contacted with ozone to bleach and delignify the pulp. The ozone stage is conducted without the addition of a peroxide bleaching agent. A chelant is introduced into the ozone stage to improve selectivity of the delignification.

[0015] In a particular embodiment, the invention relates to a process of treating a wood pulp. In an ozone stage, the pulp is contacted with ozone to bleach and delignify the pulp. The ozone stage produces hydrogen peroxide. A chelant is introduced into the ozone stage to tie up trace metals in the pulp and reduce decomposition of the hydrogen peroxide, thereby improving selectivity of the delignification.

[0016] In another particular embodiment, the invention relates to a prior process of treating a cellulose-lignin pulp in which, in an ozone stage, the pulp is contacted with ozone to bleach and delignify the pulp. The ozone stage produces hydrogen peroxide which decomposes to produce first free radicals, and the first free radicals activate decomposition of the ozone to produce second free radicals. The first and second free radicals cause degradation of the cellulose. The present invention improves the prior process by introducing a chelant into the ozone stage to reduce decomposition of the hydrogen peroxide, thereby reducing production of the first free radicals. In turn, this reduces activation of the decomposition of the ozone and production of the second

free radicals. The reduced production of the first and second free radicals improves selectivity of the delignification by reducing degradation of the cellulose.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] This invention relates to an improved process of ozone bleaching and delignification of a cellulose-lignin pulp. The process may be applicable to any type of pulp made from a lignocellulosic material, such as pulps made from different types of plants that contain primarily cellulose and lignin. In a preferred embodiment, the pulp is a wood pulp. More particularly, in some embodiments the wood pulp is a chemical pulp or a recycle pulp. The process is usually suitable for use with pulp having any consistency. In some embodiments, where the pulp comprises a suspension of the cellulose-lignin material in water, the pulp has a consistency within a range of from about 0.2% to about 50% cellulose-lignin material by weight of the pulp.

[0018] The pulp is contacted with ozone to bleach and delignify the pulp during what is referred to herein as the "ozone stage". The ozone is applied to the pulp in any suitable manner. Typically, the pulp is fed into a reactor and ozone is injected into the reactor in a manner sufficient for the ozone to bleach and delignify the pulp.

[0019] The bleaching and delignifying of the pulp is conducted in the ozone stage without the addition of a peroxide bleaching agent. In a preferred embodiment, the ozone is the only bleaching/delignification agent used during the process. However, this does not exclude any peroxide which may be formed as a by-product during the process. The bleaching and delignifying of the pulp may also be conducted without the addition of cyanamide or cyanamide salt.

[0020] The process of ozone bleaching and delignification is improved according to the invention by introducing a chelant into the ozone stage along with the ozone and the pulp. The introduction of the chelant improves the selectivity of the delignification of the pulp, so that the ozone bleaches and delignifies the pulp without significantly degrading and weakening the cellulosic fibers of the pulp. Any suitable chelant(s) can be used in the invention, such as phosphonate chelants, ethylene-

diaminetetraacetic acid (EDTA), and/or diethylenetriamine pentaacetic acid (DTPA). The phosphonate chelants are generally preferred for use in the invention. Some nonlimiting examples of phosphonate chelants are the Dequest[®] 2010 Series based on hydroxyethylidene 1,1-diphosphonic acid which are manufactured by Solutia Inc., St. Louis, Missouri.

[0021] The chelant(s) can be introduced into the pulp in any suitable amount. Generally, the pulp during the ozone stage comprises a suspension of the cellulose-lignin material (e.g., wood fibers) in water, and the chelant is introduced into the pulp in an amount within a range of from about 1 to about 100 times the total trace metals (by weight), more specifically from about 10 to about 50 times.

[0022] The selectivity of the delignification is improved compared to the same process without the chelant. Preferably, the selectivity is improved by at least about 10%, and more preferably by at least about 20%. The selectivity can be defined in any suitable manner. For example, the selectivity can be defined as $\Delta K/\Delta V$, where ΔK is the change in kappa number that measures delignification and ΔV is the change in viscosity that characterizes carbohydrate depolymerization. Alternatively, the selectivity can be defined as $\Delta K/\Delta V$ where ΔK is the change in permanganate number that measures delignification, as measured in a test that uses potassium permanganate, KMnO_4 . These selectivity definitions and the associated tests are well known in the paper manufacturing industry.

[0023] The ozone bleaching and delignification process of the invention can be conducted using any suitable process conditions. For example, in some embodiments the pulp is reacted with the ozone for a time within a range of from about 1 second to about 5 hours, or more specifically from about 10 seconds to about 10 minutes. In some embodiments, the pulp is reacted with the ozone at a temperature within a range of from about 20°C to about 90°C, or more specifically from about 20°C to about 35°C. In some embodiments, the pulp is reacted with the ozone at a pH within a range of from 1 to about 7, or more specifically from about 2 to about 6.

[0024] The pulp treated in the process may include trace metal(s) in the suspension and the chelant may function to tie up the trace

metals. The process may include the additional steps, before the ozone stage, of determining the species of trace metal and/or the amount of trace metal in the pulp, and then selecting the chelant type and/or chelant dose to match the trace metal based on the trace metal determination. The pH of the ozone stage may also be adjusted depending on the determination of species and amount of trace metals.

[0025] While not intending to be limited by theory, it is believed that the following mechanisms be involved in the improved selectivity resulting from the process of the invention. Ozone delignification produces hydrogen peroxide as a by-product of the reaction with lignin. At acid conditions common to the ozone stage, hydrogen peroxide decomposes to produce several free radical species, most of which react rapidly with lignin or pulp indiscriminately. This decomposition of hydrogen peroxide will occur faster and tend to produce worse free radicals for cellulose degradation if trace metal contamination is present. It is thought that the decomposition of hydrogen peroxide in acid conditions can be blocked by the addition of a chelant in the ozone stage. By preventing hydrogen peroxide decomposition, the harmful free radicals are not generated. The chelant addition should also tie up any trace metal ions that are present that would also cause decomposition of the hydrogen peroxide. Improving selectivity by stabilizing hydrogen peroxide in the ozone stage is a surprising finding in view of the prevailing theory in the pulping industry that the destructive free radicals are a by-product of the ozone reaction with lignin.

[0026] Moreover, it is believed that there is another potentially even larger source than the decomposition of hydrogen peroxide for the destructive free radicals. If the proper activator is present, ozone will also decompose to very reactive non-selective free radicals. Free radicals from the decomposition of hydrogen peroxide are activators for ozone decomposition to free radicals. Once started the cycle is self-sustaining until all the ozone is depleted. The free radicals produced by the decomposition of ozone and hydrogen peroxide are very reactive and non-selective. Thus the conventional theory that ozone reacts with lignin to produce free radicals seems to be correct in the end result, but neglects the important intermediate steps that can be controlled. The conventional theory is that the free radicals are a direct result

of the lignin reaction with ozone, and since the goal is to react ozone and lignin, then the production of the harmful free radicals cannot be prevented. However, by stabilizing the decomposition of hydrogen peroxide in the present invention, we block the initiation step of the ozone decomposition to free radicals which should make ozone delignification more efficient and more selective. The process of the invention is therefore believed to be novel and surprising.

EXPERIMENTS

[0027] A first set of experiments was run on northern mixed hardwood kraft pulp. A second set of experiments was run on southern pine kraft pulp. Both brown stock pulps were oxygen delignified in the laboratory prior to ozone application. Both pulps were ozonated at greater than 40% consistency with one exception.

[0028] The results of the hardwood experiments are given in Table A below.

Table A
Northern Mixed Hardwood Ozone Treatment

Sample	Permanganate Number	% Delignification	Ozone Consumption	ISO Brightness	Viscosity, cps.	Selectivity $\Delta K/\Delta V$
Brown Stock	11.2					
Oxygen Delignified	6.3	43.75		58.23	17.6	
Ozone Control	3.5	44.44	0.506	73.96	12.7	0.58
Ozone with Chelant	3.4	46.03	0.506	74.35	14.5	0.93

[0029] All experiments were made in the rotavapor reactor with 0.70% applied ozone. The chelant (Dequest[®] 2010) was applied at an unusually high application rate of 2.6%. The selectivity term is the change in permanganate number divided by the change in viscosity for the stage. Permanganate number was used for this pulp because it is a more accurate test for low lignin pulps. The increase in selectivity was considered very good.

[0030] The results of the softwood experiments are shown below in Table B.

Table B
Southern Pine Ozone Treatment

Sample	Kappa Number	% Delignification	Ozone Consumption	ISO Brightness	Viscosity, cps.	Selectivity $\Delta K/\Delta V$
Brown Stock	47.7					
Oxygen Delignified	19.9	58.28		28.32	17	
Ozone Control	15.0	24.67	0.53	36.67	12.3	1.06
Ozone w/ 75 ppm Ch.	14.1	28.90	0.42	37.09	12.3	1.24
Ozone w/ 150 ppm Ch.	14.0	29.58	0.43	38.26	12.1	1.22
Ozone w/ 225 ppm Ch.	14.3	27.92	0.42	39.19	12.5	1.25
Ozone control	14.6	26.71	0.41	37.53	12.0	1.07
Ozone w/ 750 ppm Ch.	16.0	19.40	0.12	34.34	14.5	1.59
Ozone control	14.5	27.36	0.50	37.31	12.0	1.11

[0031] All runs were made with 0.65% ozone applied. All experiments were made in a hand-shaken 2 liter flask because of problems with the rotavapor reactor. Because of the large volume of chelant added for the 750 ppm experiment, the consistency was reduced to 28.3%. The lower consistency is the likely reason that the consumption was lower. Better mixing would likely have helped increased the ozone consumption. Also ozone application was less than targeted and expected. The improvement in selectivity is not as great as for the hardwood experiments, but it is still significant.

[0032] The experiment using 750 ppm of chelant also included an unusually high dosage of chelant. Later, we realized that both samples potentially were contaminated with relatively large amounts of copper. Copper is thought to be one of the most harmful metals for causing decomposition of hydrogen peroxide. Thus we were very fortunate to have some very high doses of chelant for both sets of experiments. It is believed that to optimize the process, it is preferred to match the chelant to the particular application considering pH and metal contamination.

[0033] In accordance with the provisions of the patent statutes, the principle and mode of operation of this invention have been described in its preferred embodiments. However, it must be understood that this invention may be practiced otherwise than as specifically described without departing from its spirit or scope.

What is claimed is:

1. A process of treating a cellulose-lignin pulp comprising:
in an ozone stage, contacting the pulp with ozone to bleach and delignify the pulp, without the addition of a peroxide bleaching agent; and
introducing a chelant into the ozone stage to improve selectivity of the delignification.
2. The process of claim 1 wherein the ozone stage produces hydrogen peroxide, and the introduction of the chelant reduces decomposition of the hydrogen peroxide.
3. The process of claim 1 wherein the pulp comprises a suspension of a cellulose-lignin material in water, and the pulp further comprises trace metals, and the chelant ties up the trace metals.
4. The process of claim 3 comprising the additional steps, before the ozone stage, of determining the species of trace metal and/or the amount of trace metal in the pulp, and then selecting the chelant type and/or chelant dose to match the trace metal based on the trace metal determination.
5. The process of claim 1 wherein the selectivity of the delignification is improved by at least about 10% compared to the same process without the chelant.
6. The process of claim 1 wherein the pulp is a wood pulp.
7. The process of claim 6 wherein the wood pulp is a chemical pulp or a recycle pulp.
8. The process of claim 1 wherein the chelant is a phosphonate.

9. The process of claim 1 wherein the pulp comprises a suspension of a cellulose-lignin material in water, and the pulp has a consistency within a range of from about 0.2% to about 50% cellulose-lignin material by weight of the pulp.
10. The process of claim 1 wherein the pulp comprises a suspension of a cellulose-lignin material in water, and wherein the chelant is introduced into the pulp in an amount within a range of from about 1 to about 100 times the total trace metals.
11. The process of claim 10 wherein the chelant is introduced in an amount within a range of from about 20 to about 50 times the total trace metals.
12. The process of claim 1 wherein the pulp is reacted with the ozone for a time within a range of from about 1 second to about 5 hours.
13. The process of claim 12 wherein the reaction time is within a range of from about 10 seconds to about 10 minutes.
14. The process of claim 1 wherein the pulp is reacted with the ozone at a temperature within a range of from about 20°C to about 90°C.
15. The process of claim 14 wherein the reaction temperature is within a range of from about 20°C to about 35°C.
16. The process of claim 1 wherein the pulp is reacted with the ozone at a pH within a range of from 1 to about 7.
17. The process of claim 16 wherein the pH of the reaction is within a range of from about 2 to about 6.

18. The process of claim 1 wherein the bleaching and delignification is conducted with the ozone as the only bleaching/delignification agent.

19. The process of claim 1 wherein the ozone stage is conducted without the use of cyanamide or cyanamide salt.

20. A process of treating a wood pulp comprising:
in an ozone stage, contacting the pulp with ozone to bleach and delignify the pulp, the ozone stage producing hydrogen peroxide; and
introducing a chelant into the ozone stage to tie up trace metals in the pulp and reduce decomposition of the hydrogen peroxide, thereby improving selectivity of the delignification.

21. The process of claim 20 wherein the wood pulp is a chemical pulp or a recycle pulp.

22. A process of treating a cellulose-lignin pulp in which, in an ozone stage, the pulp is contacted with ozone to bleach and delignify the pulp, the ozone stage producing hydrogen peroxide which decomposes to produce first free radicals, and the first free radicals activating decomposition of the ozone to produce second free radicals, the first and second free radicals causing degradation of the cellulose;
the improvement comprising introducing a chelant into the ozone stage to reduce decomposition of the hydrogen peroxide, thereby reducing production of the first free radicals, thereby reducing activation of the decomposition of the ozone and production of the second free radicals, and thereby reducing the degradation of the cellulose to improve selectivity of the delignification.

23. The process of claim 22 wherein the pulp is a wood pulp.