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(54) **PROCESS OF BLEACHING A WOOD PULP**

Related U.S. Application Data

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(57) **ABSTRACT**

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A process of bleaching a wood pulp includes contacting the pulp with ozone to delignify the pulp in an ozone bleaching stage. A phosphonate chelant is added to the pulp so that the chelant is present with the pulp during the bleaching stage. The process excludes washing of the pulp to remove chelant between the chelant addition and the bleaching stage.

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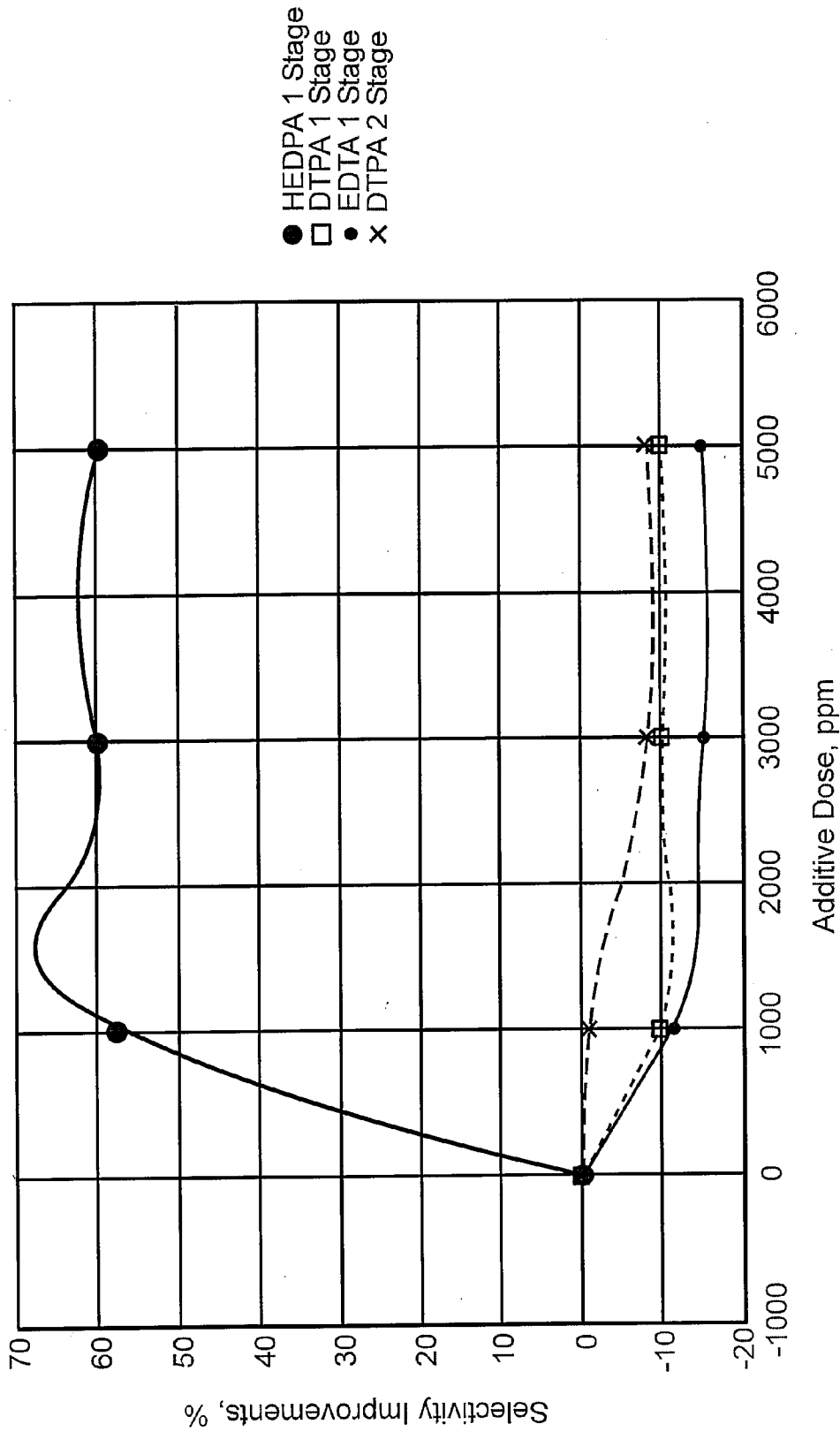


FIG. 1

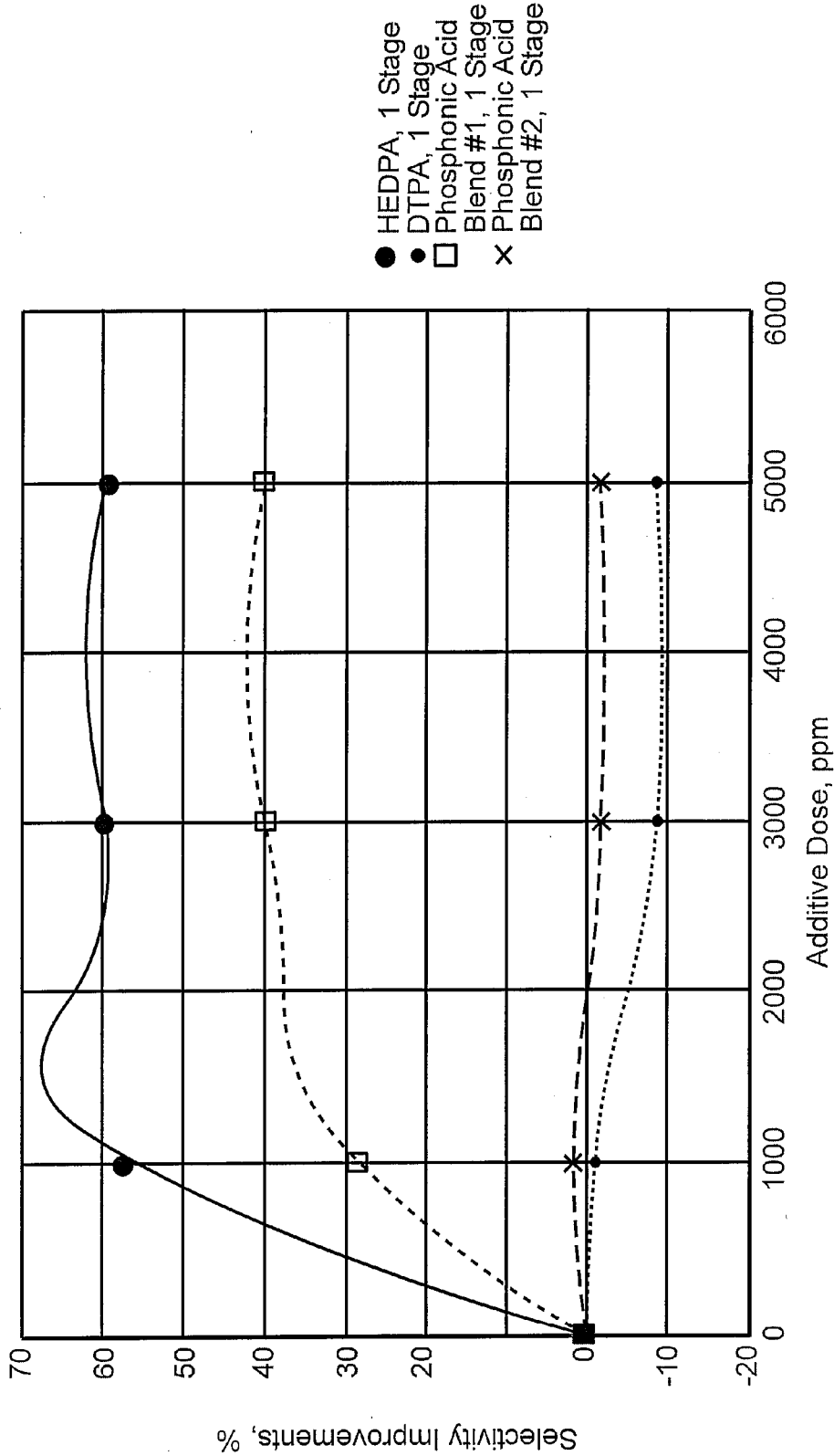


FIG. 2

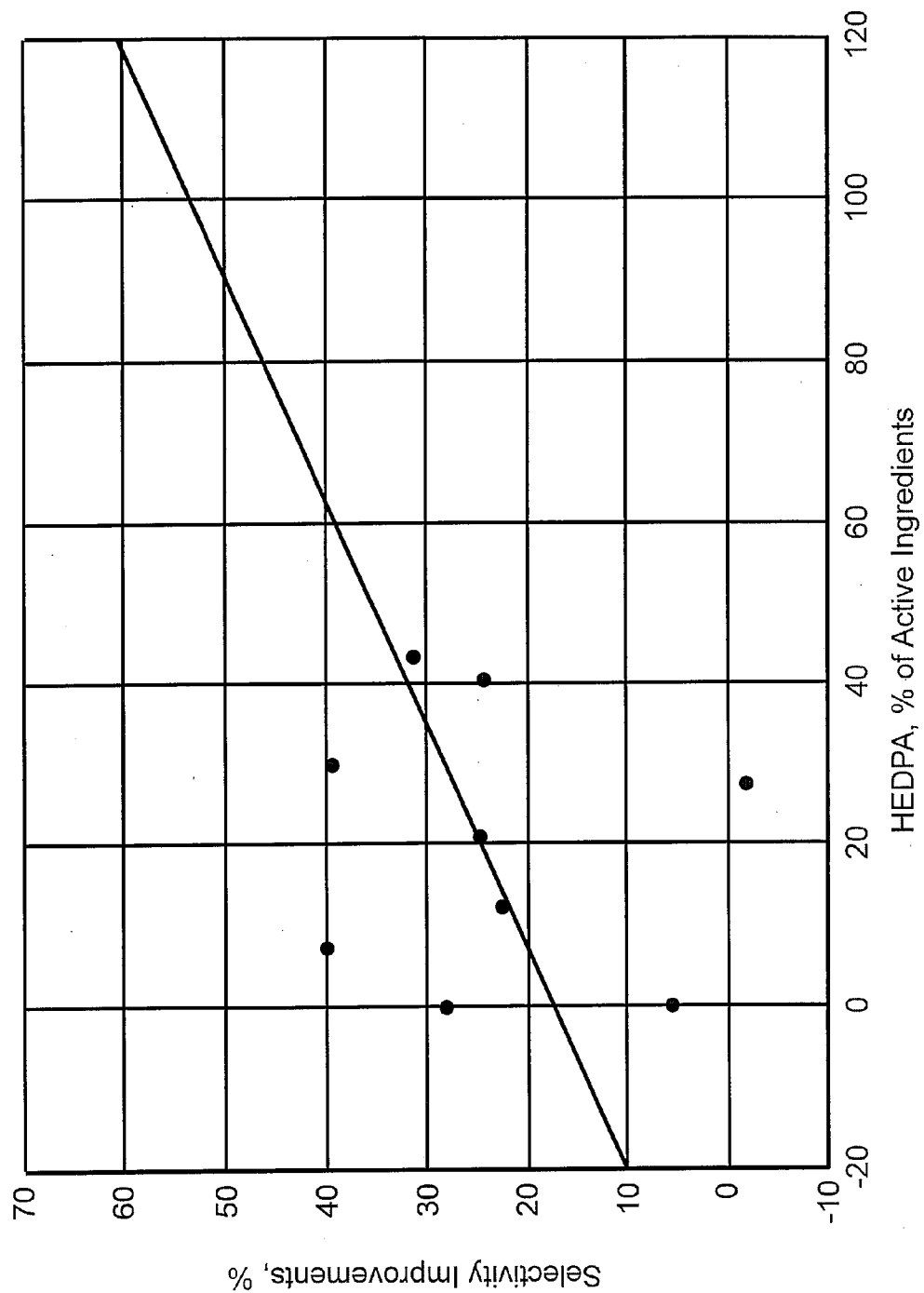


FIG. 3

PROCESS OF BLEACHING A WOOD PULP

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of U.S. application Ser. No. 11/300,126, filed on Dec. 14, 2005, currently pending, which is incorporated by reference herein.

BACKGROUND OF THE INVENTION

[0002] This invention relates in general to processes for treating lignocellulosic materials, and in particular to a process for bleaching a wood pulp.

[0003] Lignocellulosic materials, such as wood, are plant materials made up primarily of cellulose, hemicellulose and lignin. The cellulose is the chief structural element and major constituent of the plants. It consists of a fibrous cellulose portion made from polymeric chains that 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. Lignin is largely responsible for the strength and rigidity of the plants. The hemicellulose is a polysaccharide that is a component of the cell walls of the plants.

[0004] 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.

[0005] 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, the pulp is subjected to a bleaching operation which includes delignification and brightening of the pulp.

[0006] Conventionally, delignification of wood pulp has been carried out with chlorine containing bleaching agents. 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.

[0007] To avoid these disadvantages, the paper industry has attempted to reduce or eliminate the use of chlorine containing bleaching agents for 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 containing agents still persist.

[0008] Ozone bleaching of wood pulp is a process that would 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 allow 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, environmental improvement is a motivation for using ozone.

[0009] A deterrent to using ozone for bleaching has been insufficient selectivity of the delignification. Selective delignification is important to ensure that lignin is removed from the wood pulp with minimal damage to cellulose and hemicelluloses, thereby producing a strong pulp. Delignification selectivity must be improved if ozone bleaching is to be accepted by the paper industry. It would be desirable to provide a process of ozone bleaching wood pulp having increased delignification selectivity.

SUMMARY OF THE INVENTION

[0010] A process of bleaching a wood pulp comprises contacting the pulp with ozone to delignify the pulp in an ozone bleaching stage. A phosphonate chelant is added to the pulp so that the chelant is present with the pulp during the bleaching stage. The process excludes washing of the pulp to remove chelant between the chelant addition and the bleaching stage.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 is a plot showing the selectivity results of experiments in which a phosphonate chelant HEDPA was compared with non-phosphonate chelants DTPA and EDTA in an ozone bleaching stage.

[0012] FIGS. 2 and 3 are plots showing the selectivity results of experiments with HEDPA and phosphonate chelant blends.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] This invention relates to an improved process of ozone bleaching a wood pulp. The process is effective for both hardwood and softwood pulps. The wood pulp may be a chemical pulp or a recycle pulp.

[0014] The process may be suitable for use with wood pulp having any consistency, which is the dry weight of the wood fibers in the pulp as a percentage of the total weight of the pulp. In some embodiments, the pulp has a consistency within a range of from about 0.2% to about 50%.

[0015] In an ozone bleaching stage of the process, the wood pulp is contacted with ozone to delignify the pulp. 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 delignify the pulp. In certain embodiments, a bleaching "stage" will consist of a mixer to mix the ozone and pulp, and a vessel to provide retention time for reaction to come to completion, followed by a pulp washing step. Any suitable equipment can be used, such as any suitable ozone bleaching equipment known to those skilled in the art.

[0016] For example, the reactor can comprise an extended cylindrical vessel having a mixing apparatus extending in the interior along the length of the vessel. The reactor can have a pulp feed port on one end of the vessel and a pulp outlet port on the opposite end. The pulp can be fed to the reactor in any suitable manner, for example, it can be fed under pressure through a shredder which functions as a pump. The reactor can also have a gas feed port for feeding the ozone gas on one end of the vessel and a gas outlet port for removing gas after reaction on the opposite end of the vessel. In certain embodiments, the pulp and ozone are fed in opposite directions through the vessel, but in other embodiments they could be fed in the same direction.

[0017] The bleaching process can include ozone as the sole delignification agent or the ozone can be used in a mixture with another delignification agent. In certain embodiments, the process is conducted without the addition of a peroxide bleaching agent; however, this does not exclude any peroxide that may be formed as a by-product during the process. Also, in certain embodiments, the process is conducted without the addition of cyanamide or cyanamide salt. When ozone is used as the sole delignification agent, this does not exclude byproducts of the reaction; for example, the gas removed after the reaction of ozone with pulp may comprise mostly carbon dioxide. In certain embodiments, the ozone is fed to the reactor as the sole gas in the feed stream, but in other embodiments, the ozone is fed along with a carrier gas such as oxygen.

[0018] Any suitable amount of ozone can be used in the ozone bleaching stage. In certain embodiments, the ozone charge during the ozone bleaching stage is within a range of from about 0.1% to about 1%, and more particularly from about 0.2% to about 0.8%. The ozone charge is the weight of the ozone as a percentage of the dry weight of the wood fibers in the pulp.

[0019] The ozone bleaching stage can be conducted using any suitable process conditions. For example, in certain 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. Also, in certain embodiments, the pulp is reacted with the ozone at a temperature within a range of from about 50° F. to about 150° F. Further, in certain embodiments, the pH of the pulp at the end of the bleaching stage is within a range of from about 1 to about 7, and more particularly from about 2 to about 6.

[0020] The process of bleaching a wood pulp according to the invention is improved compared to earlier processes by adding a phosphonate chelant to the pulp so that it is present with the pulp during the ozone bleaching stage. The phosphonate chelant can be added to the pulp in any suitable manner. For example, the chelant can be added to the pulp by introducing it into a pulp feed stream prior to the reactor. Alternatively, it can be added by introducing it into the reactor after the pulp has been fed into the reactor, either by adding the

chelant directly into the reactor or by adding it to a process stream that feeds into the reactor.

[0021] Any suitable phosphonate chelant or mixtures of different phosphonate chelants can be used in the process. Some nonlimiting examples of phosphonate chelants include ethane 1-hydroxy diphosphonates (e.g., 1-hydroxy ethylidene-1,1-diphosphonic acid) (HEDPA), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. In certain embodiments, the phosphonate chelant comprises an ethane 1-hydroxy diphosphonate either alone or in a mixture with another phosphonate chelant. For example, ethane 1-hydroxy diphosphonate chelants are commercially available as the Dequest® 2010 series of chelants manufactured by the company formerly known as Solutia Inc., St. Louis, Mo., now doing business as ThermPhos.

[0022] The phosphonate chelant can be added to the pulp in any suitable amount. In certain embodiments, the chelant is added to the pulp so that it is present during the bleaching stage at a concentration within a range of from about 50 ppm (50 mg chelant/L water in the pulp) to about 12,000 ppm (12,000 mg chelant/L water in the pulp), and more particularly from about 500 ppm to about 3,000 ppm.

[0023] In contrast to some earlier processes that include both chelant addition and ozone bleaching of wood pulp, the present process excludes washing of the pulp to remove chelant between the chelant addition and the ozone bleaching stage. The earlier processes add chelant to sequester trace metals and then wash the pulp to remove the chelant and metals before the ozone bleaching. Thus, in contrast to the earlier multi-stage ozone bleaching processes, the present process is a single-stage ozone bleaching process because no washing occurs between the chelant addition and the ozone bleaching stage.

[0024] In certain embodiments, the addition of the phosphonate chelant to the ozone bleaching stage improves the selectivity of the delignification by at least about 10% compared to the same process without the chelant. In certain particular embodiments, the selectivity of the delignification is improved by at least about 20%, at least about 30%, at least about 40%, at least about 50%, or at least about 60%. 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.

EXPERIMENTS

Experiment 1

[0025] FIG. 1 is a plot showing the results of experiments in which wood pulp was bleached in an ozone bleaching stage, and a chelant was added to the pulp stream entering the bleaching stage, with no washing of the pulp between the

chelant addition and the ozone bleaching. A phosphonate chelant HEDP was compared against non-phosphonate chelants DTPA and EDTA. All these bleaches were done on the same pulp source (northern mixed hardwood, 8.1 permanganate number, and 28.6 cps. pulp viscosity), at the same ozone application (0.5% on pulp), for the same retention time (5 minutes), at the same temperature (110° F.), the same consistency (30%), and approximately the same final pH (3 to 4 pH). Very clearly the HEDPA outperforms the DTPA and EDTA when the additive is present during ozonation in a single stage (HEDPA 1 stage, DTPA 1 stage, and EDTA 1 stage curves).

[0026] This plot also shows a curve (DTPA 2 stage) where the pulp was pretreated with DTPA for a short time (approximately 30 minutes) and then washed before ozonation. Again, the selectivity is not improved.

Experiment 2

[0027] We have also compared several phosphonic acid blends and the first of these comparisons is shown in FIG. 2. All four of the additives were used in the single stage ozone bleach. The DTPA single stage run is shown for bracketing purposes. The HEDPA run was made with a product where all of the "active" agent in the complexing solution was HEDPA. Blend #1 was the best performer of the 9 blends that we tried, and Blend #2 was the worst performer of the blends. Generally the phosphonic acid blends are better than EDTA and DTPA, but not as good as HEDPA.

Experiment 3

[0028] The graph in FIG. 3 expands on the comparison of phosphonic acid blends. For this comparison, we have taken the maximum selectivity improvement for each of the 9 blends and pure HEDPA, and plotted that maximum improvement against the percentage of HEDPA in each mixture. From this graph, we see that HEDPA has the most effect on improving selectivity. In some cases, the addition of specialty phosphonic acids has less deleterious effects on selectivity than other blends.

[0029] In accordance with the provisions of the patent statutes, the principle and mode of operation of this process have been described in its preferred embodiments. However, it must be understood that this process may be practiced otherwise than as specifically described without departing from its spirit or scope.

What is claimed is:

1. A process of bleaching a wood pulp comprising:
 - in an ozone bleaching stage, contacting the wood pulp with ozone to delignify the pulp; and
 - adding a phosphonate chelant to the pulp so that the chelant is present with the pulp during the bleaching stage;
 the process excluding washing of the pulp to remove chelant between the chelant addition and the bleaching stage.
2. The process of claim 1 wherein the phosphonate chelant comprises an ethane 1-hydroxy diphosphonate.
3. The process of claim 2 wherein the phosphonate chelant comprises a blend of a second phosphonate chelant with the ethane 1-hydroxy diphosphonate.

4. The process of claim 2 wherein the phosphonate chelant consists solely of the ethane 1-hydroxy diphosphonate.

5. The process of claim 1 wherein the phosphonate chelant is present during the bleaching stage at a concentration within a range of from about 50 ppm to about 12,000 ppm.

6. The process of claim 5 wherein the chelant concentration is within a range of from about 500 ppm to about 3,000 ppm.

7. The process of claim 1 wherein the ozone charge during the ozone bleaching stage is within a range of from about 0.1% to about 1%.

8. The process of claim 7 wherein ozone charge is within a range of from about 0.2% to about 0.8%.

9. The process of claim 1 wherein the ozone bleaching stage is conducted at a temperature within a range of from about 50° F. to about 150° F.

10. 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.

11. The process of claim 10 wherein the selectivity of the delignification is improved by at least about 30%.

12. The process of claim 1 wherein the ozone bleaching stage excludes a peroxide bleaching agent.

13. The process of claim 12 wherein the ozone bleaching stage excludes all delignification agents besides the ozone.

14. The process of claim 1 wherein the pH of the pulp at the end of the bleaching stage is within a range of from about 1 to about 7.

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

16. A process of bleaching a wood pulp comprising:

in an ozone bleaching stage, contacting the wood pulp with ozone to delignify the pulp, the ozone charge during the ozone bleaching stage being within a range of from about 0.1% to about 1%; and

adding a phosphonate chelant which comprises an ethane 1-hydroxy diphosphonate to the pulp so that the chelant is present with the pulp during the bleaching stage;

the process excluding washing of the pulp to remove chelant between the chelant addition and the bleaching stage;

the process improving the selectivity of the delignification at least about 30% compared to the same process without the addition of the chelant.

17. The process of claim 16 wherein the phosphonate chelant consists solely of the ethane 1-hydroxy diphosphonate.

18. The process of claim 17 wherein the chelant concentration is within a range of from about 500 ppm to about 3,000 ppm.

19. The process of claim 18 wherein ozone charge is within a range of from about 0.2% to about 0.8%.

20. The process of claim 19 wherein the ozone bleaching stage is conducted at a temperature within a range of from about 50° F. to about 150° F.

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