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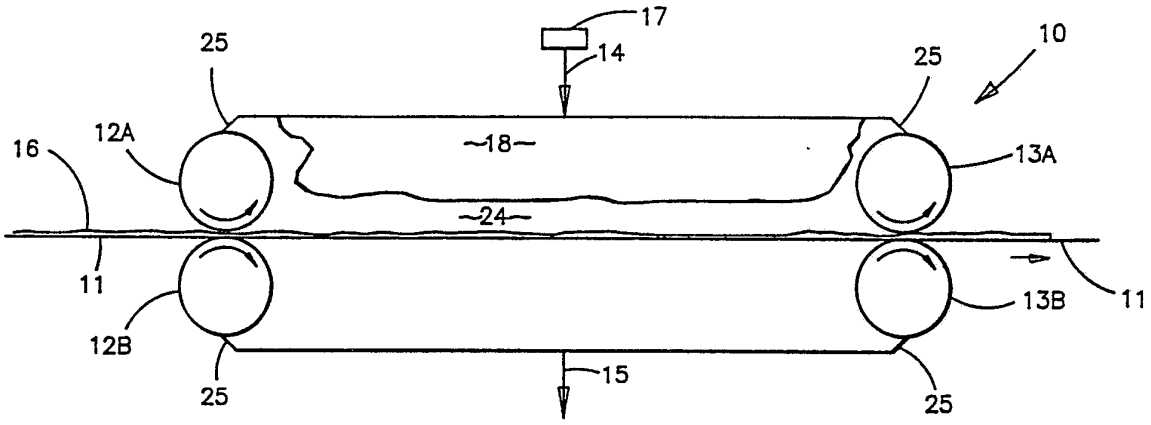

(57) Abstract

An improved apparatus and processor for delignifying lignocellulosic material (16) are disclosed in which the material has a consistency of 15 percent or greater and is contacted with the chlorine dioxide gas (14) to delignify the material, is then treated by direct alkaline extraction in the absence of an intermediate washing step to produce a delignified material with substantially reduced level or adsorbable organic halides (AOX). The effluent discharge from the bleaching process of the present invention has less than about 2.0 kg adsorbed organic halides (AOX) per ton of wood pulp. The improved apparatus employs a movable supporting web (11) for the lignocellulosic material that is gas-porous.

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PROCESS FOR GAS PHASE DELIGNIFYING LIGNOCELLULOSIC MATERIAL

The present invention relates to an improved method and apparatus for delignifying lignocellulosic material, such as wood pulp, and more specifically to the improved apparatus and improved method for gas phase delignifying lignocellulosic pulp using chlorine dioxide followed by direct alkaline extraction.

Chlorine dioxide has found wide use as a disinfectant in water treatment/purification applications, as a bleaching agent in pulp and paper production, and in a number of other uses because of its high oxidizing power.

Chlorine dioxide in solution has been used to brighten and produce a clean pulp in paper manufacture. However, it has generally been felt that the use of liquid chlorine dioxide in the first stage of a multiple stage bleaching process is not as effective as is using chlorine as a delignifying agent. However, the use of elemental chlorine has the undesireable effect of producing organo-chlorine compounds, which are measurable as adsorbable organic halides (AOX), in the effluent steams of processing facilities. Hence, as efforts have continued to focus on ways to eliminate or substantially reduce AOX discharge, chlorine dioxide has continued to be a popular agent in pulp processing, but as a brightening agent.

There are a number of chlorine dioxide generator systems and processes available in the marketplace. Most of the very large scale generators utilize a chlorate salt, a chloride ion source or reducing agent, and a strong acid. In the presence of chloride ions and acid, the chlorate ion reacts to produce a mixture of chlorine and chlorine dioxide. The chlorine present in these processes is an undesired by-product which adds to the AOX concentrations in discharge flow streams.

Many processes have been developed to produce chlorine dioxide with lower chlorine concentrations by adding a reducing agent. Some reducing agents which have been used in these applications include methanol or other organic compounds, sulfur, sulfur dioxide or other sulfur-oxygen species having a sulfur valence of less than +6, and carbon monoxide. When organic compounds are used, unreacted volatile organics, including organic acids, are present in the product gas. Using sulfur containing reducing agents, the sulfate or sulfuric acid produced accumulates as a waste product. When gaseous reducing agents, such as sulfur dioxide or carbon monoxide, are employed, reactor designs and process control systems must protect against unreacted reducing agent leaving the system with the chlorine dioxide gas.

Chlorine dioxide has been produced in prior art processes from chlorate salts by the addition of an excess of the acid used. While this acid is slowly neutralized by the accumulation of alkali metal ions that enter the process with the chlorate salt, the accumulation of salts must be removed as a waste stream. This waste stream is either liquid or solid in every process currently practiced commercially.

The preparation of chlorine dioxide from chloric acid has been accomplished to avoid the formation of an acidic alkali metal salt. Chloric acid is, however, not commercially available, although its preparation has been taught in U.S. Patent 3,810,969 issued May 14, 1974 to A.A. Schlumberger. Schlumberger teaches a process for producing chloric acid by passing an aqueous solution containing from 0.2 gram mole to 11 gram moles per liter of an alkali metal chlorate such as sodium chlorate through a selected cationic exchange resin at a temperature from 5° to 40°C. The process produces an aqueous solution containing from 0.2 gram mole to about 4.0 gram moles of $HClO_3$ per liter.

K.L. Hardee et al, in U.S. Patent No. 4,798,715 issued January 17, 1989, describe a process to produce chlorine dioxide by electrolyzing a chloric acid solution produced by passing an aqueous solution of an alkali metal chlorate through an ion exchange resin. The electrolysis is carried out using an electrocatalytic cathode where the catalyst is, for example, one or more valve metal oxides which may be combined with a platinum group metal oxide, or a platinum group metal, or oxides of a platinum group metal, magnetite, ferrite, or mixed metal oxides.

The electrolyzed solution contains a mixture of chlorine dioxide and chloric acid, which is fed to an extractor in which the chlorine dioxide is stripped off. The ion exchange resin is regenerated with hydrochloric acid and an acidic solution of an alkali metal chloride formed. Such processes require the regeneration of the ion exchange resin with acid to remove the alkali metal ions and the use or treatment and disposal of the acidic salt solution. Also the concentration of chloric acid that can be produced by an

ion exchange process is limited since more concentrated chloric acid solutions attack the ion exchange resins used in the process. Lastly, the production of chloric acid by means of a cation exchange resin is not economically attractive.

Gas phase bleaching with chlorine dioxide has been proposed over the years in various patents and publications as a method of reducing the bleaching time while cutting chemical costs. Gas phase bleaching is carried out on higher consistency pulp using mixtures of chlorine dioxide and steam and/or inert gases such as air or nitrogen.

U.S. Patent No. 3,725,193, issued April 3, 1973 to R.M. DeMontigny et al., describes a process for bleaching high consistency pulps, which includes preheating the pulp by direct steaming. A gaseous mixture of chlorine dioxide diluted with steam or a non-reactive gas is then passed through the pulp. The contact period is in the order of a fraction of a second. The bleached pulp was then held in a retention vessel for 30 minutes. Unreacted chlorine dioxide was removed from a bleaching tower by aeration. The final pH of the bleached pulp was 5.2.

Advantages alleged for gas phase bleaching of high consistency wood pulps include superior control of bleaching because of the short retention times employed; reduced chemical usage for the same brightness; and low water usage and effluent volume. The lack of a process for generating chlorine dioxide gas instantaneously or by a process having inconsequential start-up times and shut-down times has blocked the successful use commercially of gas phase bleaching. A process has been found that produces chlorine dioxide gas which can be used directly from the generator without requiring the

formation and storage of dilute aqueous solutions of chlorine dioxide which are subsequently stripped or which do not have significant concentrations of elemental chlorine gas that damage the cellulose. After delignification there is substantially no residual chlorine dioxide requiring recovery or disposal.

A recent process to reduce the AOX discharges from pulp mills has been disclosed by the Amcor Research and Technology Center in Australia which uses an oxygen pretreatment step to passivate the pulp and enhance the reactivity of liquid chlorine dioxide applied in a first stage delignification operation, followed immediately by an alkaline extraction stage without an intermediate washing step. This process substantially reduces the AOX discharge, but still requires the pretreatment step. There exists the need for a simplified process and apparatus to directly delignify lignocellulosic material with gaseous chlorine dioxide.

These problems are solved in the process of the present invention and in the design of the bleaching apparatus of the present invention by providing a reaction chamber with a moving web that delivers the lignocellulosic material to and through the reaction chamber and a process for delignifying the material which comprises contacting the lignocellulosic material with chlorine dioxide gas and conducting a direct alkaline extraction without intermediate washing to dramatically reduce the AOX discharge.

It is an object of the present invention to provide an improved apparatus for delignifying lignocellulosic material.

It is another object of the present invention to provide a first stage treatment with gaseous chlorine dioxide that dramatically reduces the AOX discharges.

It is a feature of the present invention that the apparatus has a gas-porous moveable web upon which the lignocellulosic material is placed and fed to a reaction chamber.

It is another feature of the present invention that first stage delignification of a lignocellulosic material is achieved by the direct alkaline treatment of the material following a gas phase chlorine dioxide bleaching treatment.

It is yet another feature of the present invention that any residual chlorine dioxide in the lignocellulosic material is reactively removed by the instant process.

It is still another feature of the present invention that lower AOX concentrations are achieved with pulps having an alkaline pH value prior to delignification.

It is yet a feature of the present invention that a uniform thickness of lignocellulosic material is fed into the reaction chamber on a gas-porous moveable web to achieve enhanced processing results.

It is an advantage of the present invention that a clean pulp material is obtained in less time and at lower cost in needed equipment when compared with conventional processes.

It is another advantage of the present invention that sequential delignification and extraction steps, which may be of a multiple stage process, are combined in a single gas phase bleaching and alkaline extraction step.

These and other objects,features and advantages are obtained by an improved apparatus for delignifying lignocellulosic material which employs a gas-porous movable web to transport a uniformly thick layer of the

lignocellulosic material into a reaction chamber where it is contacted with gaseous chlorine dioxide to delignify the material and then transport it directly to an alkaline extraction location. Further, a process is provided whereby the lignocellulosic material having a consistency of about 15% or greater is contacted with the chlorine dioxide gas that contains less than about 18% by weight elemental chlorine to delignify the cellulosic material and immediately thereafter extracts the delignified material with an alkaline solution in the absence of an intermediate washing. The delignified material is then separated from an effluent whereby the effluent contains less than about 2.0 kg adsorbable organic halides (AOX) per ton of lignocellulosic material.

The objects, features and advantages of the invention will become apparent upon consideration of the following detailed disclosure of the invention, especially when it is taken in conjunction with the accompanying drawings wherein:

FIG. 1 is a side elevational view of the improved gas phase delignifying apparatus showing the movable web with a portion of the side housing broken away;

FIG. 2 is a side elevational view of an alternative embodiment of the improved apparatus with the side housing broken away showing the use of multiple compartments for gaseous phase delignification; and

FIG. 3 is a side elevational view of an alternative embodiment of the improved gas phase delignifying apparatus showing the use of multiple moving webs.

Suitable pulps which can be bleached include any of those which are commonly used such as chemical kraft,

sulfite or mechanical and recycle pulps. Pulp having any suitable consistencies may be delignified including those of about 15 percent or higher, for example, from about 25 to about 60 percent can be treated by the process of the present invention. The pulps are preferably shredded or fluffed.

Chlorine dioxide gas used as a reactant in the process of the present invention contains low concentrations of elemental chlorine and preferably small amounts of inert gases, such as nitrogen or air. Suitable chlorine dioxide gas used in delignification of pulp is a mixture of chlorine dioxide, gaseous oxygen, and water vapor. Partial pressure of chlorine dioxide in the gas stream is between about 10 to 100 mm Hg. The chlorine dioxide gas has a low elemental chlorine content of less than about 18 percent. The chlorine dioxide gas can also be substantially free of chlorine, having less than about 3 percent by weight, preferably less than about 2 percent by weight, and more preferably less than about 1.5 percent by weight based on the weight of chlorine dioxide in the gas. The gaseous mixture contains varying concentrations of oxygen and water vapor. The amount of oxygen can be independently varied to provide molar ratios of O_2 to ClO_2 by volume of from about 1:4 to about 50:1. Water vapor or steam is preferably the primary diluent in the gaseous mixture and replaces other inert gases which are normally used. As a diluent, steam supplies heat to the pulp and minimizes cooling by evaporation which occurs when, for example, air is used as the diluent.

Gaseous mixtures containing chlorine dioxide suitable for use in the novel process of the present invention preferably can be produced from concentrated solutions of chloric acid.

Conversion of the chloric acid to chlorine dioxide can be accomplished, for example, by cathodic reduction in an electrolytic cell or by contacting the chloric acid with a suitable catalyst in the presence of heat. In an alternative process, highly acidic aqueous solutions containing chlorate ions, including chloric acid, perchlorate ions and hydrogen ions are reacted to produce a gaseous mixture of chlorine dioxide, oxygen and water vapor (steam). The gaseous mixture has low concentrations of inert gases, such as air or nitrogen. The aqueous solutions have an acid concentration of at least 2 molar, preferably at least 3 molar, and a concentration of chlorate ions of at least 0.02 molar and preferably from about 0.1 to about 3 molar. These acidic solutions preferably are substantially free of ionic impurities such as chloride ions, alkali metal and alkaline earth metal ions.

The hydrogen ion concentration from acid in the aqueous solutions may be provided by non-oxidizable inorganic acids such as sulfuric acid, phosphoric acid, chloric acid or perchloric acid. Preferably, the acidic solutions are reacted in the presence of a catalyst which promotes oxygen evolution.

Suitable as oxygen-evolving catalysts are, for example, metals and oxides of the elements of Group VIIIA of the Periodic Table of Elements. Thus metals such as the platinum group metals including platinum, palladium, iridium, rhodium or ruthenium; and mixtures or alloys of these platinum group metals may be employed. Additionally oxides of platinum group metals such as iridium, rhodium or ruthenium, as well as mixtures of these oxides with platinum group metals or alloys of these precious metals could be suitably employed. Likewise, iron alloys such as stainless

steel, nickel or nickel based alloys, and cobalt based alloys can be used as oxygen-evolving catalysts in the process of the invention. Other oxygen-evolving catalysts include semiconductive ceramics known as perovskites. To suppress or minimize the auto-oxidation of chloric acid to perchloric acid, for example where an oxygen-evolving catalyst is employed, it is preferred to use, as the source of chlorate ions, a mixture of chloric acid and a non-oxidizable inorganic acid in which the concentration of chloric acid is low, for example, less than about 20 percent by weight of the aqueous solution providing chlorate ions. These processes for generating chlorine dioxide can be started up in a few minutes and similarly stopped in a short time so that storage of ClO_2 gas or dissolution in water or a solvent is not required.

High purity concentrated chloric acid solutions are produced by the oxidation of high purity hypochlorous acid solutions. One process suitable for producing the chloric acid solutions heats a hypochlorous acid solution, containing from about 35 to about 60 percent by weight of HOCl, at a temperature in the range of from about 25 to about 120°C. Another process for producing the high purity chloric acid solution utilizes anodic oxidation of the high purity concentrated hypochlorous acid solution in an electrolytic cell having an anode compartment, a cathode compartment, and a cation exchange membrane separating the anode compartment from the cathode compartment.

In operation, this process includes feeding an aqueous solution of hypochlorous acid to the anode compartment, and electrolyzing the aqueous solution of hypochlorous solution at a temperature of from about 0° to about 40°C to produce the chloric acid solution.

Chloric acid solutions can be produced by these processes in any concentrations desired up to about 45% by weight of $HClO_3$. However, preferred concentrations are those in the range of from about 30 to about 40% by weight of $HClO_3$.

Generation of the chlorine dioxide gas from the reaction mixture containing chloric acid and the non-oxidizable inorganic acid is preferably conducted at atmospheric pressure in the presence of a diluent gas, such as oxygen, nitrogen or air. The temperature of the reactor mixture should not exceed 120°C, more preferably not more than about 90°C, to avoid decomposition of the chlorine dioxide in the gas phase. Where subatmospheric pressures are utilized, for example, pressures can be in the range of from about 15 to about 750, preferably from about 100 to about 500, and more preferably from about 150 to about 300 mm of Hg. At these pressures the temperature of the reaction mixture is in the range of from about 40°C to about 90°C, and preferably from about 50°C to about 80°C. The temperatures and pressures for subatmospheric pressures are selected to maintain continuous boiling of the reaction mixture.

The chlorine dioxide gas generator must be in water balance to operate in steady state conditions. The rate of heat addition to the generator determines the quantity of water that is evaporated to maintain steady state concentration, it is necessary to evaporate water continuously at about the same rate at which water is added, with the chloric acid feed solution adjusted for water formed by reaction of the chloric acid.

Alternately, chlorine dioxide gas can be obtained from commercially available generators directly producing gaseous chlorine, or by removing the gas prior to going to an adsorber for liquifaction, such as those

available from Albright and Wilson Americas under the model names R-8, R-9 and R-10, or from other suppliers of similar commercial equipment.

The novel delignification process of the present invention may, but does not require, use of traditionally employed apparatus, such as a bleaching tower. The initial delignification step of unbleached lignocellulosic material or pulp is accomplished with the use of gaseous chlorine dioxide produced by one of the aforementioned processes. The gaseous chlorine dioxide has low concentrations, or is substantially free, of elemental chlorine and is combined with a direct alkaline extraction step in the absence of an intermediate washing to reduce the AOX concentrations in the discharge stream. Delignification of the lignocellulosic material or pulp is effected in the initial stage of a multi-stage bleaching process, but may also occur as in any "D" stage. For example, delignification may also occur in the third stage for both kraft and sulfite pulps, as well as in the fifth stage for kraft pulps. The initial delignification step of unbleached lignocellulosic material or pulp may be carried out in any suitable equipment in which the unbleached pulp can be contacted with the chlorine dioxide gas. For practical reasons any reactor should be gas tight. Suitable gas tight equipment includes, for example, agitated mixers, static mixers, ribbon blenders, steam chests, high consistency shear mixers, MC pumps, MC mixers, high velocity pipe lines, fluffers, etc.

The preferred apparatus for accomplishing at least the initial delignification step is shown in Figure 1 in side elevational view as a first stage bleaching apparatus, indicated generally by the numeral

10, which has a movable and gas-porous web 11 extending therethrough. Movable web 11 can either be horizotally positioned or angled from the horizontal, to facilitate the feeding of the lignocellulosic material or pulp 16 into the reaction chamber 24. A second web 11A, seen in Figure 3, may be employed to hold the pulp material 1G in place. The reaction chamber 24 has an upper infeed roll 12A and a lower infeed roll 12B that are rotatably mounted to the apparatus housing to both support and move the web 11 therethrough. Upper exit roll 13A and lower exit roll 13B perform similar functions to remove the treated pulp material 16 from the reaction chamber 20 after a suitable contact period of the pulp material 16 with the chlorine dioxide gas. The upper infeed roll 12A and the exit roll 13A also serve to maintain the lignocellulosic or pulp material layer 16 in a uniformly thick configuration. The material 16 as placed on the entry end of the movable web 11 by suitable apparatus to assure generally even height. The material 16 may be treated in one of at least two ways prior to placement. It may be pulled from a dilute slurry of diluted pulp through a screen and expressed to the desired consistency or the water may be removed to the desired consistency and shredded or fluffed prior to being placed into a mat on the web 11.

The chlorine dioxide gas is fed from the desired supply means via the chlorine dioxide infeed means, indicated by the numeral 14 into the reaction chamber 24, seen below the partially broken away side housing 18 of the apparatus 10. A suitable gas analyzer 17 can be employed to determine the gas content and concentration to ensure proper control of the chlorine dioxide feed rate. A spectrographic method of analysis can be employed. The gas analyzer 17 will also be included or

combined with an inert gas detection device. The chlorine dioxide infeed means 14 includes a metering device to feed the gaseous chlorine dioxide into the reaction chamber, using either single or multiple injection ports or infeed locations (not shown), to obtain the required gas flow to effect the delignification. It is also possible that a back pressure type of control can be coupled with the infeed means, such as a flame arrestor or other suitable equipment.

Partial pressure of the chlorine dioxide in the chlorine dioxide gas must be limited to about 100 mm of mercury, to ensure stability. If the chlorine dioxide gas is generated under a vacuum in the generator, it must be maintained under a vacuum to ensure that it is drawn through the layer of material 16 as that layer is drawn through the reaction chamber 24. Although not shown, where a vacuum is used a vacuum pump, steam ejector or similar device may be necessary. A separate device may also be employed to remove residual chlorine dioxide after the gas has been drawn through the layer of pulp material 16 and the web 11. The reaction chamber 24 of the apparatus 10 must be sealed in a gas-tight manner from the surrounding atmosphere and may employ suitable lip seals 25 adjacent the infeed rolls 12A and 12B and the exit rolls 13A and 13B.

The positioning of the lignocellulosic material layer 16 on the gas-porous web 11 in a uniformly thick layer ensures that the active chlorine dioxide gas passes uniformly through all of the material so that uniform contact times are achieved. The layer can be a suitable thickness from two millimeters to a foot or more in thickness, more preferably from about a ¼ to about an inch in thickness, depending on the throughput

required and the gas pressure forcing the chlorine dioxide through the combined material layer 16 and movable web 11. The material 16 should be in the range of about 20 to about 50% consistency, and more preferably about 30% consistency.

The material layer 16 can spend from about 5 seconds to about 45 minutes in the reaction chamber 24, preferably from about 5 seconds to about 5 minutes, and more preferably from about 5 seconds to about 1 minute contact time in the reaction chamber 24 before exiting.

The gas-porous supporting web 11 and 11A is made of any suitable material that is highly resistant to oxidation and has sufficient strength to support the weight of the lignocellulosic material or pulp. The web 11 and 11A preferably will be in the form of a mesh screen. It can be formed of a plastic material, such as polyethylene terephthalate (PET) or other appropriate material that uses a fiber reinforced resin or is coated with such.

The passage of the chlorine dioxide and gas through the lignocellulosic material or pulp can be controlled so that it passes through at least one time, and possibly as many as two or three or more times, such as by the use of pressure differential between the upper inlet side and the lower outlet side before the gas exits through the reaction chamber 24. Multiple compartments, such as is seen in Figure 2, as may be employed where the chlorine dioxide is fed into the reaction area by the chlorine dioxide inlet ports 21. A first compartment 19 and a second compartment 20 may be separated from each other by a chamber wall 22 that is appropriately sealed against the material layer 16. It is possible that the movable web 11 could be passed in a serpentine or convoluted path through the reaction

chamber 24 to expose the material layer 16 to the chlorine dioxide gas for the appropriate required time within the reaction area.

The gaseous chlorine dioxide could contact the material layer 16 from both sides of the web 11 and or web 11A by having material layer 16 move vertically through the reaction chamber 24. The webs 11 and 11A with the intervening layer of pulp can move either cocurrently or countercurrently with the flow of chlorine dioxide gas. The webs 11 and 11A can be wound about supports or rollers (not shown) positioned on opposing sides of the reaction chamber 24 at different heights between the chamber's inlet and outlet to achieve the aforementioned convoluted or serpentine path. The webs 11 and 11A could also be twisted or inverted at each roller of different height to expose alternating surfaces of the material layer 16 to the flow direction of the chlorine dioxide gas.

Once the lignocellulosic material or pulp layer 16 has exited the apparatus 10, it then is passed directly to an alkaline extractor apparatus (not shown) to undergo the alkaline treatment. Although it is preferred that the alkaline extraction occur without any intermediate washing in the process of the instant invention, it is possible to use the apparatus 10 in conjunction with an intermediate wash.

The ClO_2 is admixed with the pulp in a reactor or apparatus 10 which is at any suitable pressure including atmospheric, subatmospheric or superatmospheric pressures. In a preferred embodiment, the reactor is at subatmospheric pressures which are preferably slightly below those employed in the chlorine dioxide generator. Optionally at superatmospheric pressures an eductor can be used which employs high

pressure air, steam or inert gases to remove chlorine dioxide from the generator and supply it to the pulp reactor. Chlorine dioxide gas is used in amounts which provide a ratio of gas to pulp treated that is suitable for delignifying the unbleached chemical pulp to the desired degree, as indicated, for example, by the selected Kappa number as determined by the Technical Association of Pulp and Paper Industry (TAPPI) test procedure T236 cm-85 approved by the Pulp Properties Committee of the process and quality division and accepted by the industry. Suitable amounts include, for example, depending on the type of pulp, those which provide a percent of ClO_2 for dry pulp determined by multiplying the Kappa number of the pulp to be treated times the Kappa factor divided by 2.63. The Kappa factor, is in the range of from about 0.05 to about 2.0.

The delignification of the pulp using the process of the invention is accomplished in surprisingly short contact times, with the delignification rate being independent of pulp temperatures. The temperature of the delignification reaction is not critical and delignification can be carried out at surprisingly low temperatures, from about ambient temperature. Temperatures in the range of from about ambient to about 90°C, preferably ambient to about 80° and more preferably, from about 20°C to about 60°C can be employed. At these temperatures minimal time is required.

To maximize the efficiency of chlorine dioxide use, delignification of the pulp normally is carried out under acidic conditions. The pH of the pulp to be treated normally is adjusted so that the final pH of the delignified pulp before alkaline extraction is in the range of from about 1 to about 6. Residual chlorine

dioxide gas can be suitably removed, such as by passing an inert gas through the pulp or sufficient residence time can be allowed to fully react the chlorine dioxide gas.

An extraction stage (E) is then carried out without an intervening washing step with, for example, caustic soda to solubilize the higher molecular weight oxidized lignins, to hydrolyze organic chlorides to salts, etc. Where chlorine dioxide has not been removed prior to extracting, a suitable reducing agent can be added with or prior to adding the extracting agents, such as sodium thiosulfate sodium sulfide, sodium sulfite, hydrogen peroxide, or combinations thereof.

The extraction is conducted at temperatures of about 60 to about 90°C, and a residence time of about 60 minutes where the final pH is 10.5 or higher. The extraction stage may include the addition of oxygen or a peroxide such as hydrogen peroxide, or a combination thereof for enhanced performance. The extracted pulp is filtered and washed to remove water soluble lignins and low molecular weight organic chlorides, among others.

After the initial delignification and extraction using the process of the present invention, the delignified chemical pulp has a Kappa number in the range of from about 1 to about 10, and preferably from about 2 to about 8. Following extraction, the viscosity of the treated pulp remains high, i.e. above about 20, indicating minimal degradation to the pulp.

The extracted pulp may be subsequently further delignified, for example, using the process of the invention or any known bleaching stage to achieve the final brightness desired.

It has been discovered that the novel process of the present invention reduces the formation of toxic by-products organic halides. These undesirable by-products, collectively identified as adsorbable organic halides (AOX), require effluents from pulp bleaching processes to undergo expensive treatment methods to eliminate AOX prior to discharge to sewers. The effluent discharge from the bleaching process of the present invention has less than about 2.0 kg adsorbable organic halides (AOX) per ton of wood pulp. AOX, as the term is used herein refers to the sum of the AOX, from the D_oE_o-stage (s). i.e. adsorbed organic halides, in effluents from the first chlorine dioxide treatment and alkaline extraction with or without washing of the pulps before extraction. The pulp produced by the present invention has a brightness and viscosity that meet or exceed the requirements of industrial papermaking.

To further illustrate the invention the following examples are provided without any intention of being limited thereby. All parts and percentages are by weight unless otherwise specified and temperatures are in degrees Celsius.

EXAMPLE 1

Chloric Acid Sourced Chlorine Dioxide for First Stage Bleaching

To a jacketed reaction vessel containing a gas distribution plate was added 100 grams of oven dried fluffed softwood pulp having a consistency of about 35% as shown in Table I. The initial Kappa number of the softwood pulp was about 29.2. The temperature of the

pulp was initially at ambient conditions and then warmed slightly to about 40°C during bleaching. The pulp reaction vessel was connected to two gas scrubbers, each of which contained a 10% solution of potassium iodide. The chlorine dioxide generator was initially filled with about 1500 grams of perchloric acid containing about 40 percent by weight of $HClO_4$, admixed with the perchloric acid was about 15 grams of ruthenium dioxide, RuO_2. A gaseous mixture of chlorine dioxide, oxygen and water vapor was generated by feeding a chloric acid solution containing about 37.16 percent by weight of $HClO_3$. During chlorine dioxide generation, the generator was maintained at a temperature between about 70 and 73°C by regulating the feed rate of the chloric acid, and by providing sufficient heat to evaporate the water present in the chloric acid solution and that formed during the generation of chlorine dioxide. The softwood pulp was treated for the time shown and during that time ClO_2 was applied equal to the Kappa Factor shown to the pulp.

The delignified was equally divided, one half to be washed and the other not washed prior to extraction (E). Where washing was employed the filtrate and the wash water were collected. Extraction of the delignified pulp was carried out by adding the indicated amount of about 3.5% NaOH at about 10% solution and water in an amount which reduced the consistency to about 10%. The pulp was held at about 70°C for about 60 minutes. The extracted pulp was dried, washed and the Kappa number determined and the viscosity of the pulp measured. The absorbable organic halides (AOX) in the combined solution mixture of the bleach filtrate, wash water, extraction liquor and wash water was determined using a commercially available DOHRMAN MC-3 analyzer and

according to Canadian Pulp and Paper Association (CPTA) standard procedure H.6P (proposed method 1991). The results from using chlorine dioxide generated from chloric acid are summarized in Table I below.

EXAMPLE 2

R-8 Generator Sourced Chlorine Dioxide for First Stage Bleaching

A similar procedure for bleaching as described above was employed for the chlorine dioxide obtained from an R-8 generator by taking the chlorine dioxide gas out of the generator prior to its being sent to an adsorber for liquifaction. The results from using the chlorine dioxide generated in this way in the above described delignification and alkaline extraction steps are summarized in Table II below.

TABLE I

SOFTWOOD PULP - KAPPA NO. 29.2

EXPER #	CONSISTENCY	pH	EXPOSURE TIME (Sec)	KAPPA FACTOR	Eo KAPPA #	Eo (ml)	WASH (ml)	AOX
1	39.3	2	52	0.143	7.4	13.3	355	0.87
1	39.3	2	52	0.143	6.7	13.3	0	0.48
5	38.7	5	66	0.146	6.5	17.5	415	0.94
5	38.7	5	66	0.146	6.4	17.5	0	0.46
9	36.3	8	34	0.089	6.9	11.2	310	0.70
9	36.3	8	34	0.089	7.7	11.2	0	0.33
15	36.3	8	53	0.089	6.4	17.5	427	0.76
15	36.3	8	53	0.089	7.1	17.5	0	0.38

TABLE II

SOFTWOOD PULP - KAPPA NO. 29.2

EXPER #	CONSISTENCY	pH	EXPOSURE TIME (Sec)	KAPPA FACTOR	Eo KAPPA #	Eo (ml)	WASH (ml)	AOX
1	39.3	2	41	0.087	6.5	17.5	500	1.16
1	39.3	2	41	0.087	6.6	17.5	0	0.67
5	38.7	5	46	0.088	5.1	17.5	465	1.45
5	38.7	5	46	0.088	6.4	17.5	0	0.72
9	36.3	8	41	0.094	7.1	17.5	435	0.77
9	36.3	8	41	0.094	7.8	17.5	0	0.39
13	39.3	2	47	0.087	6.4	18	430	1.27
13	39.3	2	47	0.087	6.7	17.5	0	0.69

This example data shows that the total AOX remaining in the filtrate after the extraction step was about one half when no intermediate washing was employed between the delignification and the extraction steps as opposed to employing intermediate washing. This held true even over a pH range of from about 2 to about 8 in lignocellulosic material and regardless of the source of chlorine dioxide. It has been found that the percent by weight of elemental chlorine in the gaseous chlorine dioxide produced from chloric acid and that obtained from an R-8 generator when passed into an iodometric solution, which measures total oxidants present, gave values that varied from less than about 3 percent to about 17.8 percent by weight. While not completely understood, it is theorized that the direct alkaline extraction in the presence of substantial quantities of elemental chlorine, such as when chlorine is used as the active agent in first stage delignification, would cause acid soluble lignins to precipitate out of solution back onto the surface of the pulp fibers. This precipitated layer would be non-reactive so that the desired brightness of the finished pulp could not be obtained. It is theorized, however, that in the absence of elemental chlorine the normally acid soluble lignins in the pulp are both acid and alkaline soluble. The use of gaseous chlorine dioxide in the first stage bleaching with high consistency pulp is believed to oxidize the lignins into soluble compounds and to break down the lignin polymer chains. Thus, when the direct alkaline extraction is used without the intermediate washing, no insoluble lignin precipitates onto the surface of the fibers to form a non-reactive alkaline insoluble surface layer. It is also possible that at high consistencies the acid soluble lignins remain inside the pulp fiber

and therefore cannot precipitate out onto the fiber surface so that the final desired pulp brightness can be obtained.

While the invention has been described above with references to specific embodiments thereof, it is apparent that many changes, modifications and variations in the materials, arrangements of parts and steps can be made without departing from the inventive concept disclosed herein. For example, in employing the improved apparatus of the present invention, it is possible that a dewatering apparatus can be incorporated into the infeed rolls. Similarly, it is possible that the direct alkaline extraction step could be accomplished with a separate compartment within the reaction chamber subsequent to contacting the pulp or lignocellulosic material with the chlorine dioxide gas. Also, scraper means could be employed in conjunction with the movable web that supports the lignocellulosic material to remove the material before or after the alkaline extraction step.

Accordingly, the spirit and broad scope of the appended claims is intended to embrace all such changes, modifications and variations that may occur to one of skill in the art upon a reading of the disclosure.

WHAT IS CLAIMED IS:

1. A process producing low adsorbable organic halides for delignifying lignocellulosic material characterized by first contacting lignocellulosic material with chlorine dioxide gas to delignify said lignocellulosic material followed by a direct alkaline extraction treatment.

2. The process of claim 1 characterized in that an alkali metal hydroxide is used in the alkaline extraction treatment.

3. The process of claim 2 characterized in that sodium hydroxide is used in the alkaline extraction treatment.

4. The process of claim 3 characterized in that a combination of sodium hydroxide and a supplemental extracting agent selected from the group consisting of hydrogen peroxide, sodium thiosulfate, sodium sulfide, sodium sulfite or combinations thereof is used in the alkaline extraction treatment.

5. The process of claim 1 characterized in that the lignocellulosic material is maintained at a consistency of about 15 percent or greater.

6. The process of claim 1 characterized in that the pressure is maintained below atmospheric pressure.

7. The process of claim 5 characterized in that the temperature is maintained at from about 20 to about 60°C.

8. The process of claim 6 characterized in that the pressure is maintained at from about 15 to about 750 mm of Hg.

9. A process for delignifying a lignocellulosic material for use in making paper characterized by contacting lignocellulosic material having a consistency of about 15 percent or greater with chlorine dioxide gas to delignify the lignocellulosic material, immediately thereafter extracting the delignified material with an alkaline solution, and separating the delignified material from an effluent, whereby the effluent contains less than about 2.0 kg adsorbed organic halides (AOX) per ton of lignocellulosic material.

10. The process of claim 9 characterized in that the pressure is maintained during delignification with chlorine dioxide at from about 15 to about 750 mm of Hg.

11. The process of claim 9 characterized in that the temperature is maintained at from about 20 to about 60°C.

12. The process of claim 9 characterized in that the alkaline extraction stage includes the simultaneous addition of oxygen to the pulp.

13. The process of claim 9 characterized in that the chlorine dioxide gas contains from about 3 to less than about 18 percent by weight of chlorine.

14. Apparatus for treating a lignocellulosic pulp material in a bleaching process, characterized by:

(a) a reaction chamber (24);

(b) a gas-porous means (11) for supporting the lignocellulosic pulp material (16), the gas-porous means (11) extending between an inlet end (12) and an outlet end (13) of the reaction chamber (24);

(c) support means (12, 13) for supporting and moving the gas-porous means (11) between the inlet end (12) and the outlet end (13) of the reaction chamber (24);

(d) compressing means connected to the reaction chamber (24) adjacent the gas-porous means (11) to compress the lignocellulosic pulp material (16) and ensure a uniformly thick layer of material on the gas-porous means (11) upon entry into the reaction chamber (24);

(e) gas infeed means (14) to feed chlorine dioxide into the reaction chamber (24) and into contact with the lignocellulosic pulp material (16); and

(f) gas withdrawal means to withdraw residual chlorine dioxide from the reaction chamber (24) after it has passed through the gas-porous means (11) and the lignocellulosic material (16).

15. The apparatus according to claim 14 characterized in that the gas-porous means (11) is a moveable gas-porous belt moving through the reaction chamber (24).

16. The apparatus according to claim 14 characterized in that the gas-porous means (11) is a mesh screen.

17. The apparatus according to claim 14 characterized in that the gas-porous means (11) is formed of an oxidation resistant material.

18. The apparatus according to claim 14 characterized in that the gas-porous means (11) is angled from the horizontal.

19. The apparatus according to claim 14 characterized in that the gas-porous means (11) is generally horizontal.

20. The apparatus according to claim 14 characterized in that the reaction chamber (24) comprises a plurality of separate compartments (19, 20).

21. The apparatus according to claim 20 characterized in that the gas infeed means (14) supplies the chlorine dioxide to the plurality of separate compartments (19, 20).

22. The apparatus according to claim 14 characterized in that the gas withdrawal means removes the residual chlorine dioxide from the reaction chamber under a vacuum.

23. The apparatus according to claim 14 characterized in that the gas-porous means (11) comprises a first (11) and a second web (11A) supporting the lignocellulosic pulp material therebetween.

24. The apparatus according to claim 23 characterized in that the first (11) and second (11A) webs move the lignocellulosic pulp material vertically through the reaction chamber (24).

25. The apparatus according to claim 24 characterized in that the lignocellulosic pulp material (16) moves cocurrently to the flow of chlorine dioxide gas.

26. The apparatus according to claim 24 characterized in that the lignocellulosic pulp material (16) moves countercurrently to the flow of chlorine dioxide gas.

27. The process of claim 1 characterized in that chlorine dioxide gas containing less than about 18 percent by weight of chlorine is used.

28. The process of claim 9 characterized in that chlorine dioxide gas containing less than about 18 percent by weight of chlorine is used.

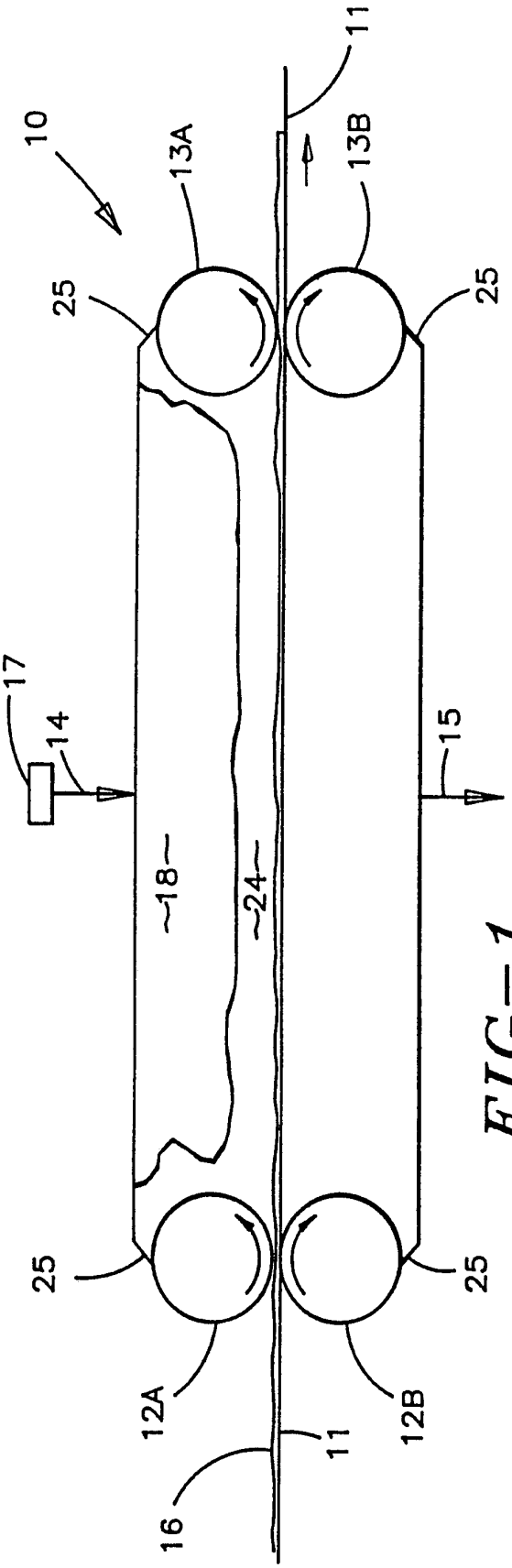
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FIG-1

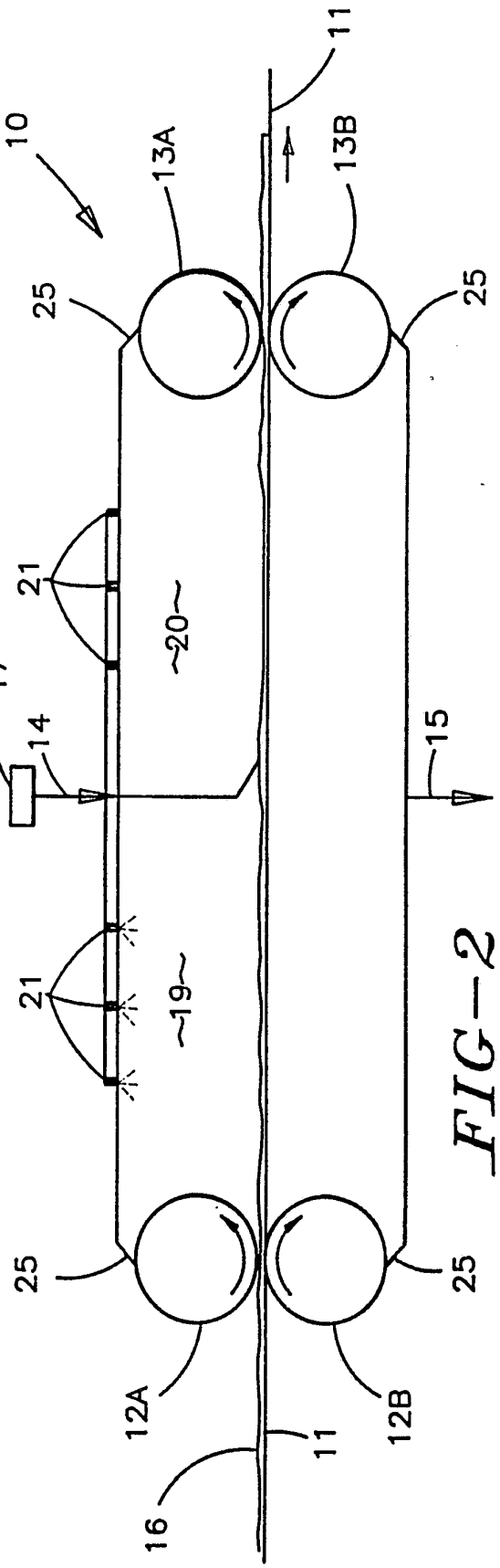
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FIG-2

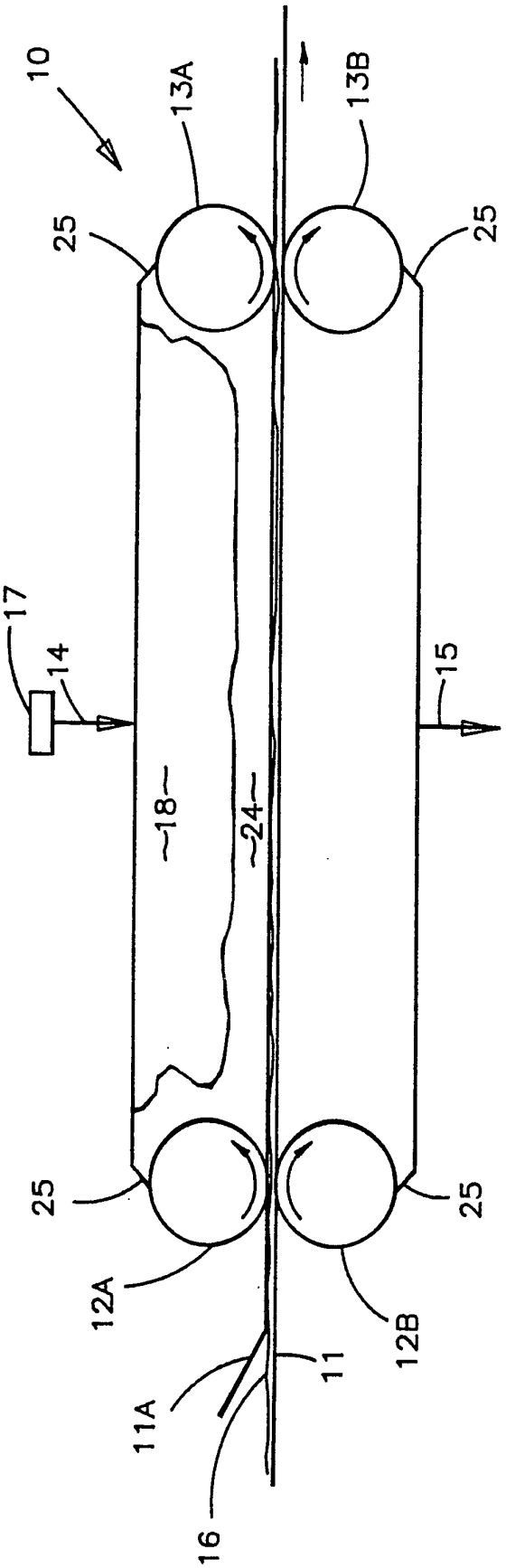

FIG-3

INTERNATIONAL SEARCH REPORT

PCT/US93/00407

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :D21C 9/14 D21C 3/02, C01B 11/02
US CL :162/65,67,89 423/478,479
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)

U.S. : 162/65,67,89 423/478,479

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 practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 3,630,828 (Liebergott et al.) 28 December 1971 See the entire document.	1-12,14-26
Y	US,A, 4,259,149 (Jaszka et al.) 31 March 1981 See the entire document.	1-12
Y	1989 Pulping Conference, Book 2, October 1989, (Basta et al.) "Low AOX, Possibilities & Consequences", page 427-436.	1-12
Y	US,A, 4,798,715 (Hardee et al.) 17 January 1989 See the entire document.	13,27-28
Y,P	US,A, 5,089,095 (Cawlfield et al.) 18 February 1992 See the entire document.	13,27-28

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 22 FEBRUARY 1993	Date of mailing of the international search report 14 APR 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer DEAN TAN NGUYEN Telephone No. (703) 308-2053

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/00407

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US,A, 5,164,043 (Griggs et al.) 17 November 1992 See the entire document.	20,22

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS
chlorine dioxide gas, Bleach, delignify, wood pulp, fiber, gas? chlorine dioxide, lignocellulos?, Hydrogen Peroxide, adsorbed organic halide#, AOX, React? chamber, belt, high consistency, mesh screen, compartment, vacuum