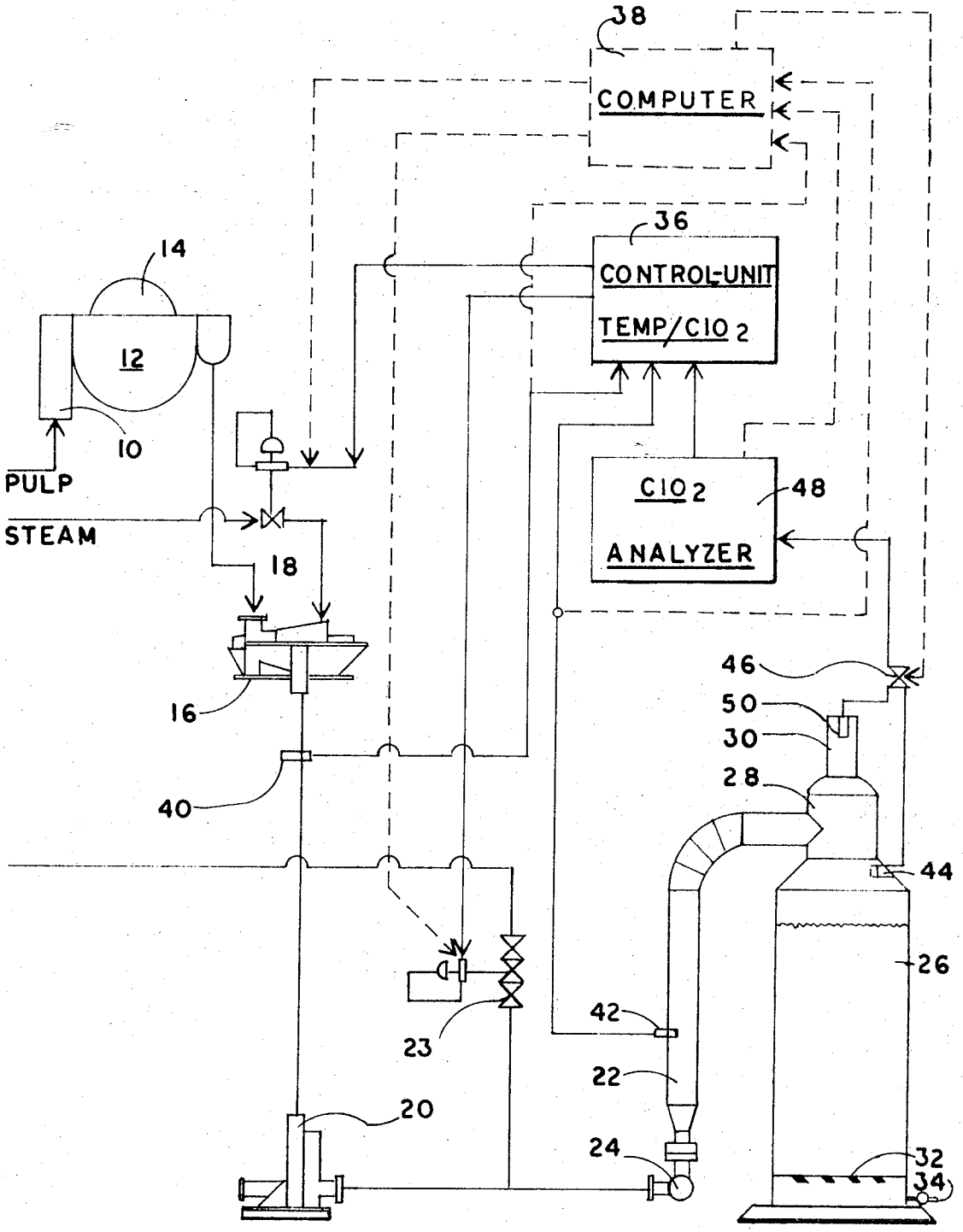
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CONTROL OF CHLORINE DIOXIDE BLEACHING

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# CONTROL OF CHLORINE DIOXIDE BLEACHING

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## ABSTRACT OF THE DISCLOSURE

Bleaching of cellulosic materials with chlorine dioxide in a conventional bleaching tower while maintaining the temperature and mass flow rate of incoming pulp substantially constant is controlled by continuously measuring the concentration of residual gaseous chlorine dioxide in the head space of the tower and adjusting the input of chlorine dioxide to achieve a residual level correlated to the desired degree of brightness.

## BACKGROUND OF THE INVENTION

This invention relates to an automatic control system for regulating the continuous bleaching of cellulosic materials and more particularly to a system responsive to the level of concentration of a gas or volatile material within a confined space above the reactants.

Positive control and regulation of the bleaching process in the pulp mill has become increasingly important because of high quality demands and high speed equipment. In a typical pulp treatment process, unbleached pulp is delignified in successive stages by treatment with chlorine, hypochlorite or chlorine dioxide and the lignins are chlorinated or oxidized to allow removal by washing and/or caustic extraction. In the final stages of the process, the cellulosic fibers of the pulp are very often treated with chlorine dioxide, in order to oxidize the fibers and achieve the desired degree of brightness. During these stages, stock is heated and mixed with chlorine dioxide and then pumped upward in a pre-retention tube into a large holding or downflow tower. At the same time, bleached pulp is continuously removed from the bottom of the tower to be washed and used in papermaking processes. The use of chlorine dioxide as a bleaching agent has become widespread in recent years due to its ability to produce high pulp brightness with a minimum of cellulose degradation. The action employed is to oxidize lignin and other colored compounds in pulp fibers with chlorine dioxide to water-soluble, or colorless materials and then remove them by washing and/or caustic extraction.

Various methods have been employed to control the variables in the continuous chlorine dioxide bleaching process. Important variables are stock consistency or concentration, lignin content, flow rate, temperature, pH, and chlorine dioxide concentration, all of which affect final brightness, directly or indirectly. Since the primary goal of the bleaching process is to obtain substantially uniform and constant brightness at a given level, it is necessary to provide means for controlling these variables within defined limits. The usual method is to take periodic samples of the pulp in order to measure and compare the initial brightness and chlorine dioxide dosage with the brightness and concentration upon completion of treatment, and to make necessary adjustments of temperature and chlorine dioxide addition on the basis of an assumed production rate. Obviously this method is unsatisfactory because a lapse of about three hours occurs before measurement, and considerable fluxuation of the variables can occur.



Proposals to overcome the deficiencies of the basic control procedure outlined above may be found in the Habrin et al. Pat. 3,051,631 and the Weyrick Pat. 3,486,971, wherein the chlorine dioxide bleaching process is controlled by measuring the oxidation-reduction potential of the pulp in the pre-retention tube immediately downstream of the zone of chlorine dioxide injection. The measurement may be made continuously between platinum-silver electrodes inserted in the flow of the pulp to monitor the reaction rate. A temperature probe is also inserted at or near the primary reaction zone in order to control the temperature of the incoming pulp. In this manner, the variables of temperature and chlorine dioxide concentration may be adjusted to achieve the desired level of brightness.

The control of the bleaching process by redox potential measurements, however, is subject to many factors which may be difficult to control and have a serious effect on the reliability of such measurements. For example, the electrodes are gradually contaminated by the pulp stream being tested and erroneous electrical readings usually result. Potential measurement may also vary with changes in the pH and temperature of the pulp, plus the chemistry of the various possible reactions between pulp contaminants and chlorine dioxide is not clearly understood, which leads to confusion concerning the effect of such reactions on redox potential. In addition, difficulties have been encountered in correlating brightness levels to potential readings, which makes it difficult to define a set point for controlling the reaction under varying conditions of temperatures and pulp consistency.

## BRIEF DESCRIPTION OF INVENTION

An object of this invention is to provide a convenient method for reliably controlling the chlorine dioxide bleaching process, said method being substantially independent of changes in pH and minor changes in temperature and pulp consistency.

In accordance with the present invention, the brightening or oxidation of cellulosic fibers is controlled by maintaining a substantially constant temperature and mass flow rate in the incoming pulp stream and then measuring the concentration of chlorine dioxide gas in the enclosed gas phase above the pulp in the bleaching tower continuously, while varying the addition of chlorine dioxide to the pulp in response to the demand indicated by said measurement. It has been found that the measurement of changes in chlorine dioxide concentration above the pulp in the bleaching tower is closely correlated to changes in the bleaching demand of the system because the gas concentration measurement is substantially unaffected by many of the system variables. For example, the residual chlorine dioxide measurement is not directly affected by changes in pH, and no elements of the sensing apparatus are in direct contact with the pulp, thereby eliminating the possibility of spurious signals because of contamination. Also, small changes in temperature of the incoming pulp do not seriously affect the validity of the measurement. Furthermore, the residual chlorine dioxide content at the top of the bleaching tower may be more closely related to actual brightness than measurement methods heretofore employed.

An additional feature of the present invention is the provision of a second gas concentration sampler in the exhaust vent of the bleaching tower, which may be employed to monitor the chlorine dioxide emitted through the exhaust. Hence, pollution control may be conveniently attained by connecting said sampler to the same analyzer as used to control the bleaching process.

## THE DRAWING

The figure is a schematic flow diagram indicating the process steps and apparatus employed in accordance with the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

The apparatus shown diagrammatically in the figure is illustrative of a continuous wood pulp treatment plant wherein the pulp has previously been substantially delignified and is in condition for final bleaching with chlorine dioxide. For example, the wood has been previously reduced to pulp form and further delignified by treatment with chlorine followed by alkali extraction. In the apparatus shown, the pulp is first washed and concentrated and then heated by steam injection. A solution of chlorine dioxide in water is then added and mixed into the heated pulp, and the mixture is pumped upward in a pre-retention tube to the top of a relatively large holding or downflow tower. The pulp is subsequently diluted near the bottom of the holding tower to enable its removal by a pump.

In the preferred embodiment shown in the drawing, a slurry of wood pulp having a 1–2% by weight fiber content is pumped through an inlet **10** into a receptacle **12** having a washing drum **14** located therein. The drum **14** picks up and washes the slurry, straining away water and waste products, such that the pulp obtains a thicker and purer consistency. The washed pulp, comprising about 12–16% fibers, is then introduced into the inlet of a mixer **16** and is mixed with steam controllably injected into the mixer through a control valve **18**. Sufficient steam is injected to raise the temperature of the pulp to within an approximate range of 140–185° F., depending upon process requirements. The heated and mixed pulp is then transferred from the mixer by a pump **20**, and is thereafter mixed with from 0.25 to 1.75% of its weight of chlorine dioxide before being introduced into the bottom of a vertically disposed preretention tube **22**.

Because chlorine dioxide ($ClO_2$) is a spontaneously explosive gas at high concentrations, means are provided to generate the gas in diluted form at the point of consumption. The $ClO_2$ may be prepared by any one of several known methods involving the reaction of sodium chlorate with a reducing agent, such as sulphur dioxide, or methyl alcohol. Chlorine dioxide is not normally used immediately and preferably is dissolved in water and stored at temperatures below 50° F. and at concentrations of less than 1%. The diluted $ClO_2$ solution is introduced through a control valve **23** into the pulp between the pump **20** and mixer **24** located at the funnel-shaped bottom inlet of the pre-retention tube **22**. The mixer **24** serves to mix the pulp with the chlorine dioxide before the hot treated pulp is forced upward in the tube.

Because of the hydrostatic head in the vertical preretention tube, the fluid pressure is greater at the bottom of the tube than at the top and may in the order of about 30 to 40 pounds per square inch, thereby aiding to keep the gas in solution and readily available for bleaching. During the retention period of the treated pulp within the preretention tube **22**, in the order of about 25 minutes or less, a majority of the chlorine dioxide oxidation reaction occurs. The pre-retention tube **22** is curved at its top and opens into the top of a downflow tower **26** at one side thereof.

The downflow tower **26** is also vertically disposed and is typically greater in height and substantially greater in diameter than the pre-retention tube **22**, so as to hold large quantities of pulp for relatively long periods of time, for example up to 2 or 3 hours. The top of the tower **26** comprises an inverted funnel-shaped vertical inlet **28** having a vent stack **30** that may be equipped with water showers and packed with a material aiding absorption of escaping excess residual $ClO_2$. A dilution ring **32** having a plurality of nozzles is provided near the base of the tower in order to return the pulp to a consistency that may be removed at the base by a pump **34**. It will also be noted that the tower **26** is normally filled to substantially a constant level below the top thereof, in order that a fixed time of confinement is provided for the bleaching pulp before its discharge to subsequent processing steps. Thus, the confined space at the top of the tower is normally held constant and pulp continuously falls from the outlet of the pre-retention tube **22** downward through said head space, while substantially an equal volume of pulp is continuously removed at the bottom of the tower by the pump **34**.



Although the bleaching process may be controlled within certain limits by varying the temperature of the pulp to be oxidized, the process is preferably controlled only by varying the addition of chlorine dioxide while maintaining the temperature of the incoming pulp at substantially a constant level. Thus, in accordance with the present invention, means are provided to regulate the addition of chlorine dioxide in response to changes in residual gaseous $ClO_2$ detected in the head space of the downflow tower **26**, while the temperature of the incoming pulp is maintained at substantially a constant level. The temperature may be maintained at a constant level by means of an automatic control device responsive to temperatures within the pre-retention tube **22** as well as temperatures at the outlet of the steam mixer **16**. The $ClO_2$ injection rate is also automatically controlled relative to a set point by a computer or other known control unit.

As shown in the drawing, the steam valve **18** and the $ClO_2$ inlet valve **23** may be adjustably operated in response to electrical impulses from a control unit **36**, or alternatively, by a digital computer **38**. The control unit **36** or computer **38** are each operable to automatically and continuously vary the additions of steam and $ClO_2$ in response to given input signals. In the case of the temperature control, a first temperature sensor or probe **40** is provided in the pulp flow at the outlet of the steam mixer and a second probe **42** is provided in a lower portion of the pre-retention tube. Preferably, the control unit **36** or computer **38** has a normally fixed set point which controls additions of steam primarily in response to temperatures measured by the first probe **40**. Adjustments may then be made to the set point in response to temperature changes detected by the second probe **42** within the reaction zone is normally employed primarily as a secondary check, because additions of various volumes chilled $ClO_2$ solution may cause upsets to this temperature and result in changes in the rate of bleaching.

The residual $ClO_2$ level is measured within the head space of the downflow tower **26** and constitutes the primary control of the bleaching process. The sensor comprises an open end sample tube **44** disposed within the aforesaid head space away from the pulp flow and connected through a multiport valve **46** to a continuous gas analyzer **48**. The analyzer is preferably of a photometric type capable of measuring $ClO_2$ concentration. Thus, a typical analyzer comprises a light source and a photometer with a windowed sample cell disposed therebetween. Analyzers of this type are available commercially, such as the Du Pont 400 Photometric Analyzer. Preferably, means are also provided to dry the $ClO_2$ gas before it enters the analyzer. The analyzer is capable of continuously analyzing the concentration of $ClO_2$ in the head space and is electrically connected to the control unit **36** or to the computer **38**. The control unit **36** or computer **38** is responsive to an excess or deficiency of $ClO_2$ and is connected to and capable of regulating the $ClO_2$ injection valve **23**.

A second sample tube **50** may be disposed within the exhaust stack **30** of the downflow tower **26** in order to provide a pollution control check on toxic $ClO_2$ being vented to the atmosphere. The sample tube **50** is connected

to a separate inlet of valve **46** (as is sample tube **44**) with a single outlet from the valve being connected to the analyzer **48**. The valve **46** is preferably a multi-port shunt valve such that sample tubes **44** and **50** as well as others can be sequentially connected to the analyzer. The valve **46** may be operated manually at intervals, or the computer **38** may be programmed to automatically switch valve **46**.

In connection with the sample tube **44** in the head space of the tower **26**, it will be appreciated that an equilibrium exists between the residual $ClO_2$ dispersed in the contained pulp and the chlorine dioxide in the gas phase above the pulp. In the event that an excess or deficiency of $ClO_2$ is present in pulp coming from the pre-retention tube **22** the equilibrium will change with corresponding increases or decreases of residual gas in the head space. Any changes in equilibrium are rapidly established because of the circulation caused by the continuous falling of the treated pulp from the pre-retention tube **22** into the tower **26**. The time lag of approximately 20–30 minutes between the addition of the $ClO_2$ and the measurement of gas concentration on the head space has not been found to be responsible for major variations in brightness, if the temperature and stock consistency is controlled within reasonable limits.

From the foregoing, it will be appreciated that residual chlorine dioxide measurements within the head space may be correlated with desired levels of brightness at various reaction (probe **42**) temperatures. In this manner, continuous adjustments may be made to $ClO_2$ additions in order to control the bleaching process in a reliable manner.

It will be understood that various changes and modifications apparent to those skilled in the art may be made to the method and apparatus of the preferred embodiment of the invention without departing from the spirit and scope of the appended claims.

Having thus described the invention, what is claimed is:

**1.** A process for continously and automatically controlling bleaching of pulp with a volatile bleaching agent wherein the pulp is first heated by steam injection, then treated and mixed with the bleaching agent, and forced upward in a pre-retention tube and into a downflow tower having a confined headspace and a vent opening therein, comprising the steps of maintaining a substantially constant temperature and mass flow rate in the incoming pulp stream, measuring the concentration of residual gaseous volatile bleaching agent in said headspace, and adjusting the injection of bleaching agent into said pulp in response to said residual gaseous volatile bleaching agent measurements to achieve a desired pulp brightness.

**2.** The process of claim **1** wherein the temperature of the pulp is maintained at a substantially constant level by measuring the temperature of the pulp at a location between the point of steam injection and bleaching agent injection and adjusting the injection of steam in response to said temperature measurements.

**3.** The process of claim **1** comprising the further step of periodically measuring the concentration of volatile bleaching agent passing through the vent opening at the top of the bleaching tower.

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