

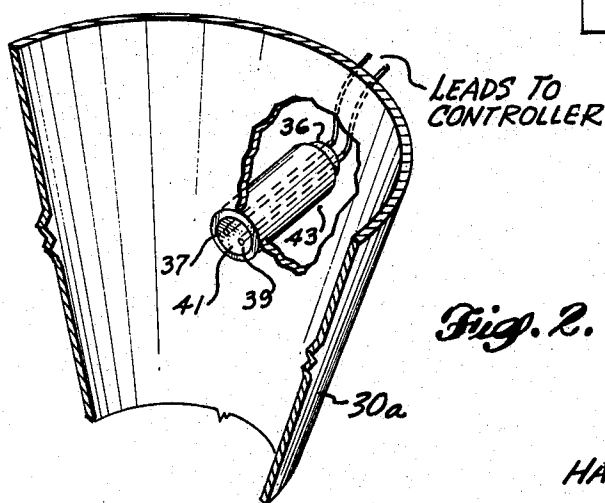
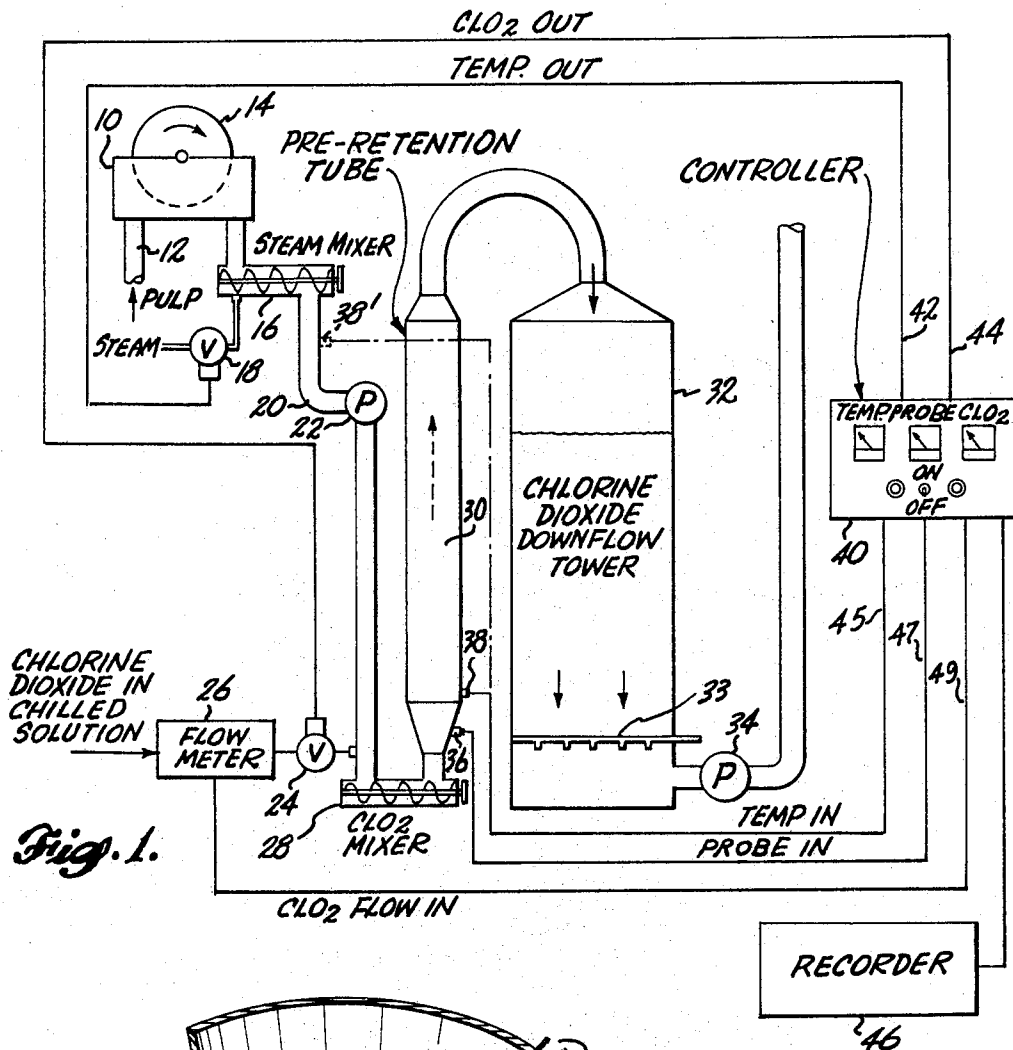
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CONTROL OF CHLORINE DIOXIDE BLEACHING

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CONTROL OF CHLORINE DIOXIDE BLEACHING

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ABSTRACT OF THE DISCLOSURE

A system for controlling chlorine dioxide bleaching of wood pulp or the like in a treatment plant wherein the pulp has been previously treated by chlorine or other primary delignification agents. The system controls the oxidation (bleaching) reaction rate by regulating application of heat and injection of chlorine dioxide in response to input measurement signals indicating the temperature of the reaction, the rate of the reaction and the rate of automatic chlorine dioxide injection on demand. A primary feature of the system is the placement of a reaction monitoring electrical probe in the pulp flow at a point immediately downstream of the point of injection of chlorine dioxide.

BACKGROUND OF THE INVENTION

This invention relates to automatic control of chlorine dioxide bleaching of cellulosic materials. More particularly, it relates to control of the rate of reaction of chlorine dioxide with wood pulp or the like in response to an electrical signal derived by monitoring the reaction rate at a point in the process following by only a few seconds the mixing of chlorine dioxide with the pulp under conditions of elevated temperature and pressure. While the invention is herein described in terms of a particular preferred form thereof, those skilled in the art will recognize various changes and modifications which may be made within the scope of the principles involved.

The basic goal in a wood pulp treatment plant is to bleach the pulp in order to achieve a given brightness or whiteness of the fiber so that it can be used in the making of paper and many other articles and substances. A typical treatment sequence involves delignification of a slurry of brown, unbleached pulp by means of chlorine, which attacks the lignins in the pulp fibers, and successively repeated further oxidation steps using hypochlorite, for example, which oxidizes the lignins and the surface of the cellulose fibers themselves, with intervening washing and caustic extraction steps for removing the chlorinated lignins from the stock, until a basic whiteness is achieved. Finally, the stock is usually treated with chlorine dioxide, which reacts primarily with the cellulose fibers themselves, oxidizing the surfaces thereof and imparting to them a higher reflectance, resulting in whiter pulp.

The apparatus used to carry out the above outlined treatments and similar bleaching techniques typically includes a series of bleaching and caustic reaction towers with intervening washing drums over which the stock is passed for removal of chlorinated lignins and the like. In the final chlorine dioxide treatment stage an upflow chemical reaction pressure tower or pre-retention tube and a downflow pressure tower are used. The present invention primarily concerns the control of this last stage of the treatment process, although the principles involved are applicable to other similar treatment processes wherein the same or similar process variables and control factors come into play. The reactions involved in the chlorine

dioxide treatment stage are recognized as quite complex and are not fully understood. Measurements and experimentation are difficult because the reactions are very rapid and take place within a confined chamber in which the reaction components are moving under conditions of elevated temperature and pressure.

The control of chlorine dioxide pulp bleaching in the past has been based primarily upon the experience of a seasoned operator who judged the quality of stock by its brightness or reflectance observed or measured at the end of the process, that is, at the bottom of the downflow tower following a transit time of two to five hours from the beginning of the reaction. Periodic samplings at this terminal point would indicate the amount of chlorine dioxide to be furnished to the pulp at the beginning point, based on such additional information as stock flow rate, strength of the chlorine dioxide, brightness of incoming stock, desired brightness at the end, and past experience. The disadvantages of this technique are quite apparent. Stock flow rate is seldom consistent, variations of plus or minus ten percent being typical. Chlorine dioxide strength may vary substantially, affecting the result of the reaction. The brightness of incoming stock is not the best indicator of the amount of chlorine dioxide required to achieve a given final brightness. The measurement point and the control point are separated along the stock flow path by a matter of hours, rendering it impossible to alter any error or imbalance as to the intervening portion of the reaction. Finally, the temperature of the reaction, an important variable, is not taken into account in such end-point observations. It is not uncommon with this technique for as much as a third of the output to be off grade—either under- or over-bright.

The brightness improvement obtained in this last stage of the pulp treatment depends primarily upon the amount of residual chlorine dioxide in the pre-retention tube, since about 85% of the reaction takes place before the pulp reaches the top of the tube. If the chlorine dioxide level is too low, then all of it will be used up before the stock reaches the bottom of the downflow tower. In that case hypochlorous acid is produced, degrading the brightness of the pulp, which must then be retreated or blended with overbright pulp. If the level of chlorine dioxide is too high, then the pulp may be overbleached and waste of the chemical occurs.

What is needed is a continuously operative automatic system for control of chlorine dioxide bleaching to eliminate such wastage, the necessity for retreatment, and other disadvantages mentioned above. It is the primary object of this invention to provide such a control system. Although control systems have been devised for other stages of the bleaching process, none of these has been found suitable for the chlorine dioxide bleaching stage because of special problems such as the necessity for temperature control and the difficulty of measuring the state of the reaction under conditions of elevated temperature and pressure. I have found that a meaningful continuous measurement indicating the state of the reaction can be taken at an early stage following introduction of chlorine dioxide into the pulp, and that this measurement in the form of an electrical signal can be used for control of the reaction rate. It is therefore a chief object hereof to provide an electrical system for controlling the rate of reaction of chlorine dioxide with fibrous cellulosic material such as wood pulp.

Another object is to provide such a control system which includes a monitoring probe placed at a point in the flow path immediately following mixing of the reagent (chlorine dioxide) with the stock to be bleached, thereby gaining a more immediate and more accurate indication of the state of the reaction and enabling immediate correction of imbalances.

A further object is to provide an electronic control system for chlorine dioxide bleaching which results in greater efficiency, less waste of pulp and bleach chemical, more uniform bleaching, and less maintenance.

A still further object hereof is to provide such a control system which obviates the need for concern with relative stock flow rate, chlorine dioxide strength, and initial stock brightness. The control system disclosed herein automatically takes changes in these variables into account and alters the process to correct imbalances accordingly.

Still another object hereof is to provide a control system for pulp treatment which operates in accordance with a predetermined program defining the required relationships between process control factors to achieve specified results.

To achieve the above ends the invention provides a technique and a system for controlling the brightening or oxidation treatment of cellulosic fibrous material by continuously and controllably applying heat to a continuous slurry, stream or mat of the material, continuously and controllably injecting an oxidizing agent into the material, continuously applying pressure to the material in the region of injection of the agent therein, deriving a first signal indicating the progress of the reaction of the agent with the material at a measurement location immediately downstream of the point of injection of the agent therein and under conditions of elevated temperature and pressure, deriving a second signal indicating the temperature of the reaction, deriving a signal indicating the rate of injection of the agent, and adjusting the application of heat and injection of the agent to effect and maintain predetermined relationships among the derived signals to increase the brightness of the material by a specified degree.

The control system according to the invention is operable to control a plant which includes means for continuously applying heat to the material to be treated as it is moved continuously through the plant, means for mixing the bleaching agent with the material when injected, means such as a vertical pre-retention tube for applying pressure to the mixture in the region immediately following mixing of the agent with the material, and means such as a downflow tower for final reaction stage processing. The control system itself comprises an electrical controller having first, second and third inputs and first and second outputs, first controllable means responsive to the first output for regulating the application of heat; second controllable means responsive to the second output for controlling injection of the agent; first, second and third measuring means coupled to the first, second and third inputs and operable, respectively, to provide electrical signals thereto indicating the state of the reaction of the agent with the material, the temperature of the reaction and the amount of agent added by the second controllable means, the first measuring means being positioned in contact with the mixture in the aforementioned region immediately following mixing of the agent with the material, that is, directly in the environment of the major portion of the bleaching reaction; and, finally, means in the controller for adjusting the application of heat and injection of the agent in response to predetermined relationships among the input signals.

Alternative positions for the second (temperature) measuring means are the immediate vicinity of the first (reaction) rate measuring means or immediately following application of heat to the material at a point "upstream" of the point of injection of the bleaching agent. In the former case the second (temperature) input of the controller automatically accounts for temperature changes in the reaction stage due to variations in the amount of agent injection, whereas in the latter case the controller itself is programmed to account for such temperature changes in accordance with the third (injection rate) input signal.

The control system preferably comprises a feedback loop wherein at least the first (reaction rate) measuring means is located downstream of the first and second controllable means regulating application of heat and injection of bleaching agent, respectively. Thus the system is operative to detect and immediately compensate for any imbalances or discrepancies from conditions required to produce the specified degree of brightness improvement. Further, the control system inherently compensates for variations in the stock flow rate, chlorine dioxide strength, and input stock brightness, rendering it unnecessary to monitor these variables separately.

An important aspect of the invention is the probe used for measurement of the reaction rate. It is specially constructed to be inserted directly in the flow path to measure the reaction under environmental conditions of elevated temperature and pressure. It includes silver and platinum electrodes and means operable to derive a signal based on the potential between the electrodes as the stock being processed is forced past them in direct contact therewith continuously.

These and other features, objects and advantages of the invention will become more apparent from the following detailed description of the preferred form of the invention, taken in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a flow diagram indicating the process steps and basic control apparatus in accordance with the invention.

FIGURE 2 is a diagrammatic representation of an electrical probe utilized in accordance with the invention to derive a signal indicative of the reaction rate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The apparatus diagrammatically shown in FIGURE 1, typical of a wood pulp treatment plant, is used herein to illustrate the preferred control system according to the invention, although the principles involved are applicable to other processes involving substantially the same variables or control factors and relationships described herein. Wood pulp in a slurry of consistency of about 1½% fiber to water (by weight) is introduced into a vat 10 through an inlet channel 12 and is passed over a washing drum 14 where water and waste products from a previous treatment stage are removed. The pulp is thicker (drier) as it passes from the washing drum through a steam mixer 16 wherein steam is injected into the pulp through a valve 18, controlled as discussed hereinafter, raising the temperature of the pulp to a controlled temperature within the approximate range of from 140° to 185° depending upon process requirements. The hot mixture, now of about 12 to 15% consistency, is pumped through the tube 20 by means of a thick stock pump 22 at a typical rate of about 4800 pounds of slurry per minute.

Chlorine dioxide (ClO_2) dispersed in water is injected into the hot pulp by an automatically controlled valve 24 from a suitable supply source, not shown. This chemical is a gas at temperatures above about 50° F. and is quite unstable. As is well known it is usually made at the consumption point by combining sodium chlorate and sulfur dioxide, for example, and used immediately or stored in solution and kept cool. In the present system it has been found practical to disperse the chlorine dioxide in water chilled to about 40° F. to maintain it in liquid form at a concentration of about 0.8 to 0.9% ClO_2 to water as it is injected into the hot pulp. Control valve 24 may vary the injection rate within a range of from 6 to 80 gallons of solution per minute or more, depending upon the demand. A typical injection rate is 40 gallons per minute at 40° F. which is approximately 384 pounds per minute. The injection rate is measured by means of flow meter 26.

Immediately upon injection into the hot pulp the ClO_2 becomes a gas and begins dispersing itself through the pulp and reacting therewith. It is further mixed into the heated slurry in a mixer 28 located at the base of a pre-retention tube 30 and its chemical reaction with the cellulose fibers is well on its way. As previously noted, about 85% of the reaction takes place by the time the pulp reaches the top of pre-retention tube 30. The remaining 15% of the reaction takes place in downflow tower 32 connected to tube 30 at the top and wherein the pulp is resident for from two to four hours during its motion toward the bottom. The pre-retention tube is typically about four feet in diameter and forty-five feet or more in height, with cone-shaped entry and exit points at its ends. The pressure at the bottom of the pre-retention tube 30 ranges from 30 to 40 pounds per square inch, while the pressure at the top may be one to two pounds per square inch. The transit time of the pulp from the ClO_2 injection point to the mixer 28 is from three to five seconds, while the transit time up the pre-retention tube 30 is 12 to 15 minutes.

The downflow tower 32 is typically greater in height than the pre-retention tube and is about 20 feet in diameter. A dilution ring 33 and outflow pump 34, along with thick stock pump 22, provide means for regulating the height of the pump column in downflow tower 32, and therefore the production rate to an approximate degree. The dilution ring 33 has numerous injection nozzles through which water is added to the bleached pulp to reduce it to pumpable consistency so that it can be removed for final washing and storage. Within the limits of this rough adjustment of production rate the actual rate of the bleaching reaction is controlled, as now to be described, by regulation of application of heat and injection of chlorine dioxide.

The quality of stock produced is judged by its brightness or reflectance, which is a measure of its purity and the oxidation that has taken place on the surface of the cellulose fibers, which in turn depends upon the amount of chlorine dioxide present in the pulp as it is pumped through pre-retention tube 30 and settles in downflow tower 32. However, I have found that the residual chlorine dioxide level can be measured at a very early stage in the reaction and the measurement can be used for control. Thus in accordance with this invention an electrical probe 36 is placed in the pulp flow at the bottom of pre-retention tube 30 and near the output of mixer 28. The probe 36 (FIGURE 2) consists of a pair of electrodes 37 and 39 mounted firmly in a solid thermoplastic cylinder 41 removably positioned in a metal sleeve 43 supported on the cone-shaped portion 30a of the pre-retention tube. The ends of electrodes 37 and 39 are platinum and silver and project directly into contact with the pulp in the region where most of the reaction takes place, that is, immediately following mixing of ClO_2 with the pulp and under conditions of elevated temperature and pressure, within 6 to 60 seconds transit time from the ClO_2 injection point, typically about 12 seconds.

The level (relative amount) of ClO_2 present in the pulp in this region is critical and is indicative of the state of the reaction. The signal obtained is generated electrolytically in the mixture of pulp and ClO_2 and typically falls within a range of from 400 to 700 millivolts, depending upon probe position, production rate, brightness to be achieved and other factors.

While it is not certain whether the probe 36 measures the oxidation-reduction potential at its location or some other combination of electrical factors in the complex chemical reaction taking place, on the basis of the signal obtained from the probe I have found that the process can be controlled with much greater accuracy and constancy than could be obtained heretofore. That is, the brightness improvement is directly related to the probe signal, and if the temperature and stock flow rate are held substantially constant, reasonable results can be obtained

simply by controlling the rate of injection of ClO_2 automatically in response to the probe signal.

However, in accordance with the preferred form of the invention, the temperature of the reaction is also used as a control variable. Accordingly a temperature probe 38 is positioned in the vicinity of reaction rate probe 36, for example about twelve inches above it. The exact location of the temperature probe is not critical so long as a signal is obtained indicative of the temperature in the region where most of the reaction is taking place. As an alternative a temperature probe 38' may be positioned near the output of steam mixer 16 under control conditions later mentioned.

The preferred control system includes a controller 40 having input terminals 45, 47 and 49 responsive respectively, to temperature probe 38, to reaction probe 36, and to the rate of ClO_2 injection as measured by flow meter 26. The controller is capable of generating control signals in first and second outputs 42 and 44 operable, respectively, to regulate application of heat to the pulp by opening or closing control valve 18, and to regulate the rate of ClO_2 injection by opening or closing control valve 24. A recorder 46, also used as a preferable but optional feature for continuous display and recording of input and output variables, may be a separate unit or a part of the control unit itself.

It is found that a higher ClO_2 level, resulting in a higher reaction probe signal, requires a higher temperature in order to cause assimilation of the additional ClO_2 . Consequently in response to an increase or a decrease in signal at input 47 the controller increases or decreases steam injection at valve 18. A higher reaction probe signal may result from a decrease in the susceptibility of the incoming pulp to oxidation, decreased stock flow rate, or increased concentration of ClO_2 in the injected solution. A lower reaction probe signal may result from greater absorption of ClO_2 into the pulp, lower concentration of ClO_2 in the injected solution, or increased stock flow rate, and calls for injection of more ClO_2 and possibly an adjustment in steam injection. For a given production rate an attempt is made to maintain substantially constant temperature when possible.

Temperature control becomes critical when accurate results are desired because the strength of the chlorine dioxide solution injected by valve 24 may vary from 0.5% to 1%, ClO_2 to water. Thus the amount of chilled water (40°) may be doubled or halved in a short period of time, since twice as much half-strength solution is required as compared with the amount of full-strength solution required to effect the same reaction rate. Typical flow rates as measured by the flow meter 26 range from 20 gallons per minute to 50 gallons per minute, depending upon the demand as indicated by the reaction probe 36. These injection rates obviously affect the temperature in the region just downstream of the ClO_2 injection point where most of the reaction takes place, in view of their very significant relationship to the total stock flow rate. The probe 38 detects these temperature changes and its output signal is used in the controller to cause a compensating adjustment in applied heat at valve 18. In that case the temperature control loop can be viewed as operating somewhat independently of the injection rate control loop, the former operating to compensate for variations caused by operation of the latter and thereby helping to attain constancy in the process.

On the other hand it is possible to program into controller 40 an automatic compensation for temperature variations in response to the output signal of flow meter 26, since the affect of given amounts of injected ClO_2 solution on the temperature of the pulp can be calculated, assuming constant solution temperature and constant stock flow rate. Thus controller 40 is programmed to adjust valve 18 automatically for different input signals at terminal 49 representing different injection rates. The injection rate itself is adjusted in response to the re-

action probe input signal at terminal 47, which in turn depends on various factors previously mentioned, so the interrelationships among the signals involved are evident.

The automatic adjustment in application of heat is better effected with a temperature probe 38' in the alternative position in channel 20 near the output of steam mixer 16. Here the temperature is more clearly controlled, since the probe is a better indication of the rate of application of heat than is the controller's own adjustment of valve 18, and since the delay due to transit time from steam mixer 16 to the reaction region is eliminated. This arrangement requires closer calibration of the controller 40, however, since a number of variations measured automatically by temperature probe 38 at the later positions are not measured by probe 38'. Of course it is possible to place probes at both positions and program the controller to respond to both.

As an example of control performance, in the final treatment of hemlock pulp already treated to a brightness of 65 GE (General Electric brightness units), at a production rate of about 9 tons per hour and specified output brightness of 80 GE (15 degree improvement), a reaction temperature of 160° F. was required and chlorine dioxide injection rates of from 0.4 to 0.45% (dry chemical to dry pulp, by weight) were found typical. A change in reaction probe signal of approximately 20 millivolts produced a change of about 3½ gallons per minute in the rate of injection of ClO₂ solution and a temperature change of about 1½° F. (If the strength of the ClO₂ solution were known, the injection rate change could be converted to a percentage, but the strength is not usually constant.) To achieve 88 GE brightness (23 degree improvement) a reaction temperature of 180° F. and injection rates of 0.7 to 0.8% were required.

The production rates, injection rates, efficiencies, responses and many other factors involved vary from plant to plant; the examples given herein are intended to be illustrative guidelines only. In accordance with the invention specified brightness improvement has been achieved consistently to within a range of plus or minus ½ GE and excess ClO₂ at the output of the process stage was reduced to substantially zero at all times.

What is claimed is:

1. In a system for controlling the bleaching of cellulosic fibrous material in which the material passes along a continuous flow path through a bleaching agent treatment stage including a steam mixer for adding steam to the material to increase its temperature, a bleaching agent mixer coupled to said steam mixer for mixing a bleaching agent with the hot material, a pre-retention tube or bleaching agent upflow tower coupled to the bleaching agent mixer and a bleaching agent downflow tower, the combination comprising

a region of reaction in a lower portion of said upflow tower adjacent said bleaching agent mixer where the mixture of hot material and bleaching agent is subjected to continuous pressure from the contents of the upflow tower,

electrical sensing means in said upflow tower and within said region of reaction for sensing the state of reaction between said bleaching agent and said material,

first valve means coupled to said bleaching agent mixer for controlling the addition of the bleaching agent to the material,

automatic control means coupled to said electrical sensing means,

means coupling said automatic control means to said first valve means to control the rate at which the bleaching agent is added to the material,

temperature sensing means within said upflow tower for sensing the temperature of the material within said region of reaction,

means coupling the temperature sensing means to the automatic control means,

second valve means coupled to said steam mixer for varying the application of heat to the material, and means coupling the automatic control means to the second valve means, whereby the reaction rate may be regulated.

2. The control system of claim 1 comprising means coupled to said bleaching agent mixer for sensing the rate at which the bleaching agent is added to the bleaching agent mixer, and means coupling the rate sensing means to the automatic control means.

3. A system for controlling the bleaching of cellulosic fibrous material moving along a continuous flow path comprising

a steam mixer for applying heat to the material moving along the path,

a bleaching agent mixer for mixing a bleaching agent with the heated material moving along the path, first coupling means coupling said steam mixer to said bleaching agent mixer,

an upflow tower in the flow path of the mixture from said bleaching agent mixer forming a region of reaction under heat and pressure of bleaching agent and material,

second coupling means coupling said bleaching agent mixer to said upflow tower,

an electrical controller having first, second and third inputs and first and second outputs,

first controllable means connected to said steam mixer and responsive to the first output of said controller for regulating the application of heat,

second controllable means coupled to said bleaching agent mixer and responsive to the second output of said controller for controlling the rate of addition of the bleaching agent to the material,

first measuring means coupled to the first input of said controller and positioned in a portion of the upflow tower adjacent said second coupling means in the region of reaction for measuring the state of the reaction of the bleaching agent with the material and generating an electrical signal proportional thereto, second measuring means coupled to the second input of said controller and positioned adjacent said first measuring means in the upflow tower for measuring the temperature of the reaction and generating an electrical signal proportional thereto, and

third measuring means coupled to the third input of said controller and to said bleaching agent mixer for measuring the amount of bleaching agent added to the material and generating an electrical signal proportional thereto,

whereby adjustments in the application of heat and the addition of the bleaching agent may be accomplished in response to predetermined relationships among said electrical signals.

4. The control system of claim 3 wherein said first measuring means comprises an electrical probe having

a platinum electrode and a silver electrode both positioned to contact the mixture in the region of reaction and

means for deriving a signal related to the electrical potential between the electrodes.

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