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PROCESS FOR BLEACHING WEBS OF FIBROUS CELLULOSE MATERIAL WITH HYDROGEN PEROXIDE VAPOR CONTAINING WATER VAPOR

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This invention relates to an improved bleaching method and particularly to a continuous method for bleaching webs of fibrous materials with hydrogen peroxide.

Alkaline hydrogen peroxide solutions are widely used for bleaching textile materials, wood pulps and the like. Such solutions are employed commercially either by applying the preformed peroxide solution to the material to be bleached or by immersing the latter in the solution. Dilute peroxide solutions are generally used for cost reasons. In some so-called "saturation" methods in which the material to be bleached is merely dampened with the bleach solution instead of immersed therein, the use of somewhat more concentrated solutions has been proposed. However, rapid and uniform application of bleach solution, whether concentrated or not, is difficult to obtain; consequently, prior saturation bleaching methods have not been as satisfactory as desired.

From a practical standpoint, it would be highly advantageous to have a continuous bleaching method which could be integrated with existing continuous methods and equipment for forming or processing continuous webs of fibrous materials such as textiles and paper. In the usual paper machine, a wet pulp sheet containing about 10% pulp (dry basis) is continuously formed on a Fourdrinier screen from which it is carried by continuous supporting felts between press rolls (usually two sets) which reduce the water content of the sheet to correspond to a pulp content of about 30 to 40%. The sheet is then passed through a dryer consisting of a large number of heated cylinders or cans over whose surfaces the continuously advancing sheet of paper is passed. During such passage, the sheet is pressed against the heated cans by means of a continuous felt, called a dryer felt. The sheet passes through the machine at rates up to around 1800 feet per minute and higher.

No bleaching method has been available heretofore which could be satisfactorily integrated with continuous paper making operations for simultaneously, continuously and uniformly bleaching paper webs. Application of a peroxide bleaching solution, e. g., by spraying, to the paper web ahead of the paper machine dryer to obtain flash bleaching in the dryer has been proposed but is far from satisfactory because uniform distribution of the peroxide is difficult to achieve by spray methods of application in the short time involved due to the high rate of travel of the web. The amount of peroxide solution that can be applied by spraying is limited because the addition of the solution weakens the web. If the solution is sprayed on at places where the web is mechanically supported, e. g., on the screen, a large portion of the bleach solution is lost by removal on the screen and in the suction boxes and press rolls, making such method prohibitively expensive.

It is an object of the invention to provide an improved continuous method for bleaching webs of fibrous materials. A further object is to provide a continuous method for bleaching such webs, wherein an aqueous solution of a

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conditioning agent and hydrogen peroxide vapor are continuously applied uniformly to the web as it is continuously advanced. A particular object is an improved and highly efficient method for bleaching paper webs which can be readily integrated with the usual paper making operation. Further objects will be apparent from the following description.

The objects of the invention are accomplished by separately and continuously applying to a moving web of the fibrous material which is to be bleached (a) a liquid comprising a non-volatile water-soluble conditioning agent, such as a non-volatile alkaline material and/or a stabilizer, and (b) hydrogen peroxide vapor, and then subjecting said web to conditions under which bleaching will occur. After application of the conditioning agent and hydrogen peroxide vapor, the web will most generally be heated to accelerate bleaching. However, heating can be omitted and bleaching can be effected at ordinary temperature over a longer period of time if desired.

Any non-volatile water-soluble conditioning agent which enhances or promotes peroxide bleaching or functions as a stabilizer for peroxide can be used. Examples are water-soluble non-volatile alkaline materials such as the alkali metal hydroxides and alkaline reacting salts thereof, e. g., caustic soda, sodium carbonate, trisodium phosphate and borax, which function primarily as alkalizing agents or alkaline buffers for promoting bleaching. Examples of stabilizers, some of which also function as alkalizing agents, are the alkali metal silicates, such as sodium silicate, and the molecularly dehydrated phosphates such as the sodium pyrophosphates, sodium tripolyphosphate and sodium hexametaphosphate; also, magnesium salts such as magnesium sulfate and silicate. These conditioning agents or mixtures thereof are applied in liquid form, e. g., as aqueous solutions. Application thereof to the web may be subsequent or prior to the application of the hydrogen peroxide vapor. Application prior thereto is generally preferred.

Application of the liquid comprising the conditioning agent can be made in any desired manner, e. g., by well-known spray or roller application methods. Use of relatively concentrated solutions of the agent is usually desirable so as to avoid introducing into the web an unduly large amount of water.

It has been found that hydrogen peroxide vapors are rapidly absorbed by the moving web, particularly when the latter is damp, so that application can be readily effected simply by contacting the moving web for a short interval of time with an atmosphere containing hydrogen peroxide vapor. Such contact can be readily effected by passing the web continuously through an enclosure containing hydrogen peroxide vapor and to which such vapor is continuously supplied as required. Alternatively, the moving web can itself be made to constitute a wall of such an enclosure whereby one side of the web will be contacted with the hydrogen peroxide vapor-containing atmosphere. It has been found that even when the vapor is contacted with only one side of the web, absorption is effective. This rapid and effective absorption of the peroxide and the fact that effective amounts of peroxide can be readily applied and absorbed without undue dilution by solvent are important and highly advantageous features of the present method.

An especially effective way of applying the peroxide is by means of a slot-type applicator positioned transversely of the moving web and in contact therewith, the peroxide vapor mixture being continuously contacted with the web through the slot. Use of such an applicator integrated with a paper machine has indicated that amounts of peroxide effective for bleaching purposes can be applied substantially quantitatively in contact times of the order of 0.2 to 0.05 second or less when using a mixture

of water and hydrogen peroxide vapors. Such rapid and efficient absorption of hydrogen peroxide is truly remarkable and makes practical its application at web speeds of up to 1800 feet per minute and higher.

Hydrogen peroxide vapor may be produced for present purposes by any convenient method, e. g., by passing a stream of an inert carrier gas such as nitrogen, air or steam, through a solution of hydrogen peroxide. In such method, the hydrogen peroxide vapor content of the resulting gaseous mixture can be controlled as desired by controlling the peroxide concentration in the solution, the temperature of the solution and the rate of gas flow. Another practical way of producing the hydrogen peroxide vapor is by vaporizing a hydrogen peroxide solution by the application of heat thereto. The hydrogen peroxide vapor content of the gas mixture used can be varied over a wide range. Absorption of the hydrogen peroxide vapor occurs rapidly and effectively even at concentrations as low as 1.0 mg. per liter, but in most applications concentrations of at least 0.5% H_2O_2 vapor by volume, preferably 1.0 to 15% H_2O_2 vapor by volume, will be employed. Higher concentrations, e. g., up to approximately 22%, can be used if desired but such higher concentrations usually will be less practical.

Application of either the conditioning agent or the hydrogen peroxide vapor can be effected at a single application station or at a plurality of such stations. Also, either can be applied to one or both sides of the moving web.

The continuously advancing web to which the above materials are applied will preferably be damp at the points of application. The free water content of the web will generally be within the range of about 5 to 70%, based upon the total weight of the damp web, a water content ranging from about 15 to 70% being preferred. Such water content may be derived by previously applying water to the web, e. g., by spray or immersion methods, or it may represent water originating from a previous processing operation, e. g., in the formation of a paper web or sheet in a paper making machine.

A distinct advantage in applying the conditioning agent and hydrogen peroxide vapor to webs containing around 5 to 70% free water is that such webs absorb the applied materials very rapidly. Another advantage is that at such moisture contents absorption of a given amount of hydrogen peroxide results in a substantially higher peroxide concentration in the web than can be obtained when the same amount of peroxide is applied by prior solution application methods. This higher concentration is important since the higher the peroxide concentration the greater will be the driving force for the bleaching reaction.

The amount of hydrogen peroxide to be applied in any instance will depend upon the amount of bleaching intended. In most cases, absorption of hydrogen peroxide equal to at least 0.01% H_2O_2 based upon the dry weight of the fibrous material will be desired. Most generally, the absorbed peroxide will range from about 0.1 to 3.0%. Absorption of such or larger amounts can be readily effected by the vapor application method of this invention. The amount absorbed will depend upon several factors including the time of contact between the web and the treating gas mixture and the hydrogen peroxide vapor content of the latter. In general, longer contact times and higher concentrations of peroxide vapor in the gas mixture increase the amount of peroxide absorbed. It has been found that absorption of amounts of peroxide adequate for most bleaching purposes can be readily effected in such remarkably short contact times as to permit integrating the bleaching operation with the usual paper making operation of a paper machine. Such integration is of great practical value in that both operations are effected simultaneously in the same equipment, with only minor changes in the paper machine being required to permit separate applications of the conditioning

agent and hydrogen peroxide vapor to the paper web as it passes through the machine.

When integrating bleaching with paper making, as indicated, the hydrogen peroxide vapor can be applied effectively at any stage following the formation of the web on the Fourdrinier screen. Application between the press rolls and the dryer, where the water content of the damp web is generally in the range of 60 to 70% will be preferred in some cases, however, application can be made if desired in the dryer, e. g., between drying cans, or following the dryer. The conditioning agent is preferably applied to the formed web in advance of the dryer, most preferably at a station in advance of that at which the hydrogen peroxide is applied. Thus, a solution of the conditioning agent may be applied, e. g., by a sprayer or roller applicator, across the width of the moving web between the two sets of press rolls just ahead of the dryer, while the peroxide vapor is conveniently and effectively applied between the last set of press rolls and the dryer. Either the conditioning agent or the peroxide vapor can be applied during formation of the web, e. g., on the Fourdrinier screen, but such practice is not generally practical because a substantial part of the materials so applied would be lost with the water removed on the screen and by the subsequent action of the suction boxes and the press rolls.

The conditioning agent, generally an alkaline material and/or a stabilizer, will be added in amounts intended to provide the desired promoting and/or stabilizing effect in the resulting bleach solution. A mixture of conditioning agents will frequently be desirable. A mixture which is usually very effective is a combination of caustic soda and a molecularly dehydrated phosphate, e. g., sodium pyrophosphate, so proportioned and added at such a rate as to result in the web containing about 0.01 to 0.5% caustic soda and about 0.1 to 1.0% sodium pyrophosphate based upon the dry weight of the fibers. However, the amounts of such agents used may be varied considerably depending upon the material being bleached, the amount of peroxide used and the bleaching conditions employed.

The invention is illustrated by the following examples.

Example 1

A newsprint paper furnish consisting of 85% unbleached groundwood and 15% unbleached sulfite pulp was continuously formed into a web of paper on a paper machine operating at a speed of about 175 feet of paper per minute. An aqueous conditioning solution containing caustic soda and sodium pyrophosphate was continuously applied uniformly across the width of the paper web on the Fourdrinier screen over the third of 4 suction boxes by means of a roller applicator. The water content of the web at the point of application was about 90%. The solution was applied at such a rate that the web as it left the last press roll before the dryer contained about 0.5% sodium pyrophosphate ($Na_4P_2O_7$) and 0.017% caustic soda ($NaOH$), based upon the dry weight of the web.

Hydrogen peroxide vapors were applied to the web at a station between the last press roll and the dryer where the water content of the web was about 60%. Application was made through two application chambers, one on each side of the web and so positioned that the advancing web constituted one side of each chamber. Each of the chambers extended across the width of the web and 6 inches along its length. A gas mixture containing about 4-5% H_2O_2 vapors by volume, 45-50% water vapor and the balance air was supplied continuously to each of the chambers. The hydrogen peroxide absorbed by the web during the short time of travel between the two chambers was 1.1% H_2O_2 , based upon the dry weight of the web.

The water content of the web following application of the peroxide was about 60%; after passage through the dryer it was about 7%. After calendering and standing

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one day in roll form, the paper had a brightness of 64.8 units compared with a brightness of 56.9 units for similar unbleached paper. Brightness values were determined using a General Electric reflectometer.

Experience has shown that the conditioning agent can be more efficiently applied between the press rolls where the water content of the web is 70–75%.

Example 2

A printing paper furnish consisting of 70% unbleached groundwood and 30% unbleached sulfite pulp was formed into paper and simultaneously bleached substantially as described in Example 1, except that the composition and rate of application of the conditioning solution were such that caustic soda and sodium pyrophosphate contents of the web were 0.5% and 0.033% (dry basis), respectively, and the point of application was just ahead of the first press roll where the water content of the web was about 85%. Also, the amount of absorbed hydrogen peroxide was 1% (dry basis). The bleached roll of paper had a brightness of 66.8 units compared with 59.2 units for a control roll of unbleached paper. Printing properties of the bleached roll were the same as for the control roll.

Example 3

The general procedure of Example 1 was repeated except that the furnish used consisted of 70% bleached groundwood and 30% bleached sulfite pulp; and the conditioning solution contained only sodium pyrophosphate, and was applied so as to give a sodium pyrophosphate content in the web of 0.5% (dry basis). After 8 days standing in the roll, the brightness of the treated paper was 71.7 units compared with 63.3 units for the control.

Example 4

The general procedure of Example 1 was repeated except that a furnish of 100% unbleached groundwood pulp was used and the absorbed H_2O_2 content of the web was 0.8–0.9% (dry basis). The brightness of the treated paper after 6 days in the roll was 66.7 units compared with 56.9 units for the untreated control.

Example 5

The general procedure of Example 1 was repeated except that the furnish was 100% unbleached sulfite pulp and the absorbed H_2O_2 content of the web was 0.75% (dry basis). After 5 days in the roll, the brightness of the treated paper was 62.3 units compared with 51.2 units for the untreated control.

In addition to the paper furnishes indicated in the examples, other furnishes composed of various combinations and proportions of the pulps indicated, as well as other paper or wood pulps which normally respond to peroxide bleaching, can be successfully bleached by the present method. Such other pulps include kraft, soda, semi-chemical, and chemigroundwood pulps. It is also applicable generally to the bleaching of any fibrous material known to be bleachable by means of hydrogen peroxide in the presence of a non-volatile water-soluble conditioning agent. In addition to paper webs, it is applicable to the bleaching of textile fabrics composed of animal, vegetable or synthetic fibers. However, since it is especially effective when employing alkaline conditioning agents, it is most useful for bleaching webs composed of cellulosic fibers, e. g. paper webs and cotton textile materials. The conditioning agent, the amount thereof used, and the bleaching conditions, e. g. temperature, will of course be chosen keeping in mind the particular type of fibrous material being bleached in any given instance. Any of the conditioning agents and bleaching conditions which are effective for a given fibrous material in prior saturation bleaching methods are generally effective in practicing the present method.

Most generally, the conditioning agent and hydrogen peroxide vapor will be applied to the web while the latter

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is at ordinary or slightly elevated temperature although the web can be at considerably higher temperatures if desired. Following their application, the web can be permitted to bleach simply by storing the same at ordinary or somewhat elevated temperature for a time sufficient for the desired bleaching action to occur. Such storage is preferably carried out under conditions minimizing vaporization of water from the web, e. g. by storing the web in a rolled-up or stacked mass. Most preferably, the web will be heated immediately after application of the peroxide vapor to accelerate bleaching. In the case of paper webs, heating by passage through the dryer of the paper machine is very effective, in which case heating and evaporation of water from the web occur simultaneously to effect substantially all or a major part of the bleaching in the dryer. However, in some instances, the paper from the dryer will still contain a substantial amount of hydrogen peroxide so that further bleaching occurs during storage of the paper roll from the dryer. Heating can also be effected under conditions such that little or no evaporation of water from the web occurs, e. g. by direct steaming. Heating without evaporation of water, e. g. by steaming, may be desirable and distinctly preferred in some instances, e. g. in cotton bleaching, where evaporation of water may result in damage to the goods.

We claim:

1. A bleaching process comprising separately and continuously applying to a moving damp web of a fibrous cellulose material bleachable with hydrogen peroxide (a) a liquid, non-volatile, water-soluble conditioning agent effective in enhancing the bleaching action of hydrogen peroxide upon said material, and (b) hydrogen peroxide vapor, said damp web containing free water equal to from 5 to 70% of its weight and said vapor being applied by contacting the moving damp web with a mixture of hydrogen peroxide vapor and at least 45% by volume water vapor for a time of from 0.05 to 0.2 second until from 0.01 to 3% hydrogen peroxide based upon the dry weight of said fibrous material is absorbed by said web, and thereafter bleaching said web with the absorbed hydrogen peroxide in the absence of any further amount of hydrogen peroxide.

2. A process for bleaching a fibrous cellulose material bleachable with hydrogen peroxide comprising continuously applying to a continuously moving damp web of said material at one application station a liquid, non-volatile, water-soluble conditioning agent effective in enhancing the bleaching action of hydrogen peroxide upon said material, said damp web containing free water equal to from 5 to 70% of its weight, continuously applying hydrogen peroxide vapor to said continuously moving web at another application station by contacting a mixture of hydrogen peroxide vapor and at least 45% by volume water vapor with said moving web for a time of from 0.05 to 0.2 second until from 0.01 to 3% hydrogen peroxide based upon the dry weight of said fibrous material is absorbed, and thereafter bleaching said web with the absorbed hydrogen peroxide in the absence of any further amount of hydrogen peroxide.

3. The process for bleaching cellulose fibers comprising separately and continuously applying to a continuously advancing damp web of cellulose fibers containing free water equal to from 5 to 70% of its weight (a) an aqueous solution of a non-volatile alkaline material effective in enhancing the bleaching action of hydrogen peroxide on said fibers, and (b) hydrogen peroxide vapor, said vapor being applied by contacting the moving web with a mixture of hydrogen peroxide vapor and at least 45% by volume water vapor for a time of from 0.05 to 0.2 second until from 0.01 to 3% hydrogen peroxide based upon the dry weight of said fibers is absorbed by said web, and thereafter bleaching said web with the absorbed hydrogen peroxide in the absence of any further amount of hydrogen peroxide.

4. The process for bleaching cellulose fibers comprising continuously applying to a continuously advancing damp web of cellulose fibers at a first application station an aqueous solution of a non-volatile alkaline material effective in enhancing the bleaching action of hydrogen peroxide on said fibers, said damp web containing free water equal to from 5 to 70% of its weight, continuously applying hydrogen peroxide vapor to said continuously advancing web at a later application station by contacting the moving web with a mixture of hydrogen peroxide vapor and at least 45% by volume water vapor for a time of from 0.05 to 0.2 second until from 0.01 to 3% hydrogen peroxide based upon the dry weight of said fibers is absorbed, and thereafter bleaching said web with the absorbed hydrogen peroxide in the absence of any further amount of hydrogen peroxide.

5. The process for bleaching cellulose fibers comprising continuously applying to a continuously advancing damp web of cellulose fibers at a first application station an aqueous solution of a non-volatile alkaline material effective in enhancing the bleaching action of hydrogen peroxide on said fibers, said damp web containing free water equal to from 5 to 70% of its weight, continuously applying hydrogen peroxide vapor to said continuously advancing web at a later application station by contacting the moving web with a mixture of hydrogen peroxide vapor and at least 45% by volume water vapor for a time of from 0.05 to 0.2 second until from 0.01 to 3% hydrogen peroxide based upon the dry weight of said fibers is absorbed, and thereafter heating said web in the absence of any further amount of hydrogen peroxide as it is continuously advanced.

6. The process of claim 5 wherein the web is composed of paper pulp.

7. The process of claim 6 wherein the solution of a non-volatile alkaline material contains a hydrogen peroxide stabilizer.

8. The process of claim 6 wherein, after application of the hydrogen peroxide vapor, the web is heated and dried as it is continuously advanced.

9. The process of bleaching paper during the continuous formation thereof on a paper making machine comprising continuously applying to a paper web during its continuous advancement through a paper making machine an aqueous solution of non-volatile alkaline material effective in enhancing the bleaching action of hydrogen peroxide on said web, said application being made between the web forming screen and the dryer of said machine, and continuously and separately applying hy-

drogen peroxide vapor to said web during its advancement through said machine by contacting the moving web with a mixture of hydrogen peroxide vapor and at least 45% by volume water vapor for a time of from 0.05 to 0.2 second until from 0.01 to 3% hydrogen peroxide based upon the dry weight of the web is absorbed, and bleaching said web with the absorbed hydrogen peroxide in the absence of any further amount of hydrogen peroxide.

10. The process for bleaching paper during the continuous formation thereof on a paper making machine comprising continuously applying to a paper web during its continuous advancement through a paper making machine an aqueous solution containing a non-volatile alkaline material effective in enhancing the bleaching action of hydrogen peroxide on said web and a hydrogen peroxide stabilizer, said solution being applied to the web at a first station in the machine between the web forming screen and the dryer, and continuously applying hydrogen peroxide vapor to said web in said machine at a second application station by contacting the moving web with a mixture of hydrogen peroxide vapor and at least 45% by volume water vapor for a time of from 0.05 to 0.2 second until from 0.1 to 3% hydrogen peroxide based upon the dry weight of said web is absorbed, said second station being subsequent to said first station, and bleaching said web with the absorbed hydrogen peroxide in the absence of any further amount of hydrogen peroxide.

11. The process of claim 10 wherein said second application station is between the last press rolls and the dryer.

12. The process of claim 10 wherein the aqueous solution applied at the first station contains caustic soda and sodium pyrophosphate.

13. The process of claim 12 wherein the aqueous solution applied at the first station contains, from 0.01 to 0.5% caustic soda and 0.1 to 1.0% sodium pyrophosphate based upon the dry weight of the web.

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