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BLEACHING OF WOOD PULP WITH A SEQUESTERING AGENT AND HYDROGEN PEROXIDE

Andrew J. Gard, 12 Orchard St., Wellesley, Mass.

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This application is a continuation-in-part of my application Serial No. 74,153, filed December 6, 1960 (now abandoned).

This invention relates to the bleaching of wood pulp and in particular to the bleaching of ground wood or mechanical pulps, and chemically modified ground wood pulps. Its principal object is to provide an improved process of bleaching with hydrogen peroxide which, in comparison with prior art processes, is both simpler and more efficient both in terms of the amount of chemicals consumed and in the quality and brightness of the pulp produced.

In conventional practice ground wood and mechanical pulps are bleached with peroxides by mixing the pulp with an aqueous alkaline solution containing the requisite amount of peroxide. Typically this solution is prepared by dissolving magnesium sulfate, sodium silicate, sodium peroxide and hydrogen peroxide in water to provide the proper balance of alkalinity and peroxide content. Generally the mixture will contain 2 to 3 percent of peroxide and 1.5 percent alkali (calculated as NaOH) and will be buffered by the presence of sodium silicate to a pH of 10.5 to 11 (all amounts being based on the weight of oven-dried pulp). The solution is typically mixed with pulp which has previously been thickened to a concentration of 14 to 15 percent solids or wood pulp by weight, and the pulp is maintained in contact with this alkaline bleaching medium in a bleaching tower for about 1.5 hours to 2 hours at a temperature between about 105° F. to 120° F.

In this process the colored constituents of the pulp are removed to a large extent. Typically eastern and western wood species common in this country will be brought from an initial brightness of 58 to 62 G-E units (as measured by the General Electric reflectometer on a scale taking pure block magnesium oxide as 100 and carbon black as 0) to a brightness of from between 72 and 78 G-E units.

A major disadvantage of this process arises from the loss of bleaching capacity which results from premature and unproductive decomposition of the peroxide in contact with the ground wood pulp.

I have now found that a seemingly slight modification of the mixing procedure will not only largely eliminate this loss of peroxide but will also result in a significant increase in the brightness of the bleached product. Basically I have found that if the peroxide is first mixed with the wood pulp under slightly acid conditions, and the alkaline components are thereafter added so as to diffuse into the pulp after the pulp has been impregnated with the peroxide, the bleaching process may be carried out much more efficiently. Accordingly the process features the addition of hydrogen peroxide as a solution having a concentration of between about 2 and 25 percent H_2O_2 by weight and a pH of less than 7, and preferably between 4 and 5.5, to a slurry containing in excess of 10 percent by weight of wood pulp. After the peroxide has been thoroughly mixed with the pulp, an aqueous solution containing the alkaline ingredients normally employed in the bleaching operation is added and mixed thoroughly with the pulp. In the mixing operations, the pulp is brought to the temperature conventionally employed, i.e., about 105° F. to 120° F. and a final pH of 10.5 to 11, as in conventional practice, and is maintained in this condition typically between 1.5 and 2 hours. There is thus a gradual diffusion of the alkaline ingredients into the wood fibriles

which has been found to promote an improved bleaching action which minimizes the decomposition of hydrogen peroxide and results in a brightness of at least 2 to 3 G-E units higher than can be ordinarily obtained.

By adding the hydrogen peroxide initially and following that with the addition of the alkaline ingredients, the alkaline solution need contain only the requisite amount of alkali, generally in excess of 1.25 parts (calculated as NaOH) per 100 parts of oven dry pulp, including the sodium silicate present to buffer the solution at the proper pH. Inasmuch as the amount of alkali required is dependent upon the amount of peroxide, where the latter is used in small amounts it may be possible to eliminate the sodium silicate altogether. This process also eliminates the sodium peroxide, which is hazardous and difficult to handle.

Inasmuch as Epsom salts are conventionally present to preserve the stability of the stock solution, the elimination of the peroxide from the solution also obviates the need of this chemical.

In the preferred embodiment of the invention, a further economy is realized by treating the pulp, prior to its being concentrated to greater than 10 percent solids, with metal sequestering agents, such as dehydrated phosphate salts and chelating agents such as the tetrasodium salt of ethylenediaminetetraacetic acid or pentasodium salt of diethylenetriaminepentaacetic acid. This pretreatment prior to thickening removes and deactivates catalytic metal ions that may be present and that otherwise accelerate decomposition of hydrogen peroxide.

Mechanical or chemico-mechanical wood pulp containing initially three percent solids after the initial screening and mechanical refining operations is first treated with a sequestering agent to eliminate free metal ions, particularly copper, iron and manganese. Typically 1 to 2 pounds of tetrasodium ethylenediaminetetraacetate are added to the pulp per 100 pounds of oven dried pulp. Following this addition, the pulp is thickened in the conventional manner to a solids concentration in excess of 10 percent, typically to 14 to 15 percent by weight by water removal, and is fed into a mixer into which is also added hydrogen peroxide in an amount of about 2 to 3 parts (expressed as of a 50 percent by weight solution of H_2O_2) per 100 parts of oven-dried pulp. This is typically added as a solution containing 2 to 25 percent H_2O_2 having a pH of 4.0 to 5.5. The ingredients are thoroughly combined in the mixer and are at the same time heated by the addition of live steam sufficient to bring the temperature to about 110° F. to 120° F. After thorough mixing the slurry is fed to a second mixer into which is introduced an alkaline aqueous solution containing preferably between 1.25 and 1.8 parts of alkali (calculated as NaOH) per 100 parts of oven-dried pulp, including sodium silicate sufficient to buffer the slurry at a pH between 10.5 and 11.

Steam may also be added to the second mixture to maintain the temperature at between 110° F. and 120° F. From the second mixer the slurry is fed to a bleaching tower where it is held for 90 to 120 minutes, and is then discharged through an outlet conduit into which is fed sulfur dioxide in an amount sufficient to neutralize the pulp and bring the pH down to 6 or lower.

By the process described above, a saving of 20 to 30 percent of the peroxide may be realized, while a pulp having a brightness of at least 2 to 3 G-E units above that realized by the conventional prior art method is produced. Moreover, the independent control of the peroxide and the alkalinity is advantageous in that the conditions required for any particular pulp are more readily produced. Where greater brightness is required, a second stage bleaching with sodium or zinc hydrosulfite may be employed, but the improved results realized from the

peroxide bleaching step alone largely eliminate the need of a second bleaching stage.

The invention is further understood from the following: If a mill withdraws water from a pulp system at 3 percent consistency, expressed on an air dry basis, which is equal to 1800 pounds of bone dry fiber plup per ton of air dry pulp, then:

$$\frac{1800}{.03} = \begin{array}{r} 60{,}000 \text{ lbs. of water and pulp (fiber)} \\ -1{,}800 \\ \hline 58{,}200 \text{ lbs. of water} \end{array}$$

On passage over a vacuum thickener, the consistency becomes 14 percent, expressed on air dry basis, thus there are removed

$$\frac{1800}{.14} = \begin{array}{r} 12{,}860 \text{ lbs. of water and pulp (fiber)} \\ -1{,}800 \\ \hline 11{,}060 \text{ lbs. of water} \end{array}$$

or

$$\begin{array}{r} 58{,}200 \\ -11{,}060 \\ \hline 47{,}140 \text{ lbs.} \end{array}$$

of water are removed to increase the consistency of the pulp system from 3 percent to 14 percent prior to impregnation with the conventional peroxide bleach solution.

If a mill is using 3 percent "Solozone" to bleach with, this means 2.4999 percent of 50 percent H_2O_2 or 1.2495 percent of 100 percent H_2O_2. On a per ton basis, this means 49.98 pounds of 50 percent H_2O_2 (roughly 50 pounds of 50 percent H_2O_2 per ton of O.D. pulp). Thus, the conventional dilution upon addition of the peroxide bleach solution made up from the above amount of peroxide is to a consistency of 11 percent to 12 percent. The amount of water containing the above number of pounds of 50 percent H_2O_2, or 100 percent H_2O_2, is determined as follows:

$$\frac{1800 \text{ lbs. of Air Dry Pulp}}{12} = \begin{array}{r} 15{,}000 \text{ lbs. of } H_2O \text{ and pulp fiber} \\ -1{,}800 \\ \hline 13{,}200 \text{ lbs. of water} \end{array}$$

Then at 14 percent consistency,

$$\begin{array}{r} -11{,}060 \text{ lbs. of water} \\ \hline 2{,}140 \text{ lbs. of water} \end{array}$$

contain the 50 pounds of 50 percent of H_2O_2, or roughly a 2⅓ percent solution of peroxide is introduced into the 14 percent consistency pulp slurry.

Although this invention has been described with reference to its presently preferred embodiments, it will be appreciated that various modifications can be made by those skilled in the art and familiar with this subject, and that all such may be made without departing from the scope of this invention. It will be observed that the invention takes advantage of the known chemistry of bleaching and resides in the order, strengths and other conditions in which the steps using more or less conventional chemicals are combined in a novel way to produce improved results not heretofore attainable. The limits for the hydrogen peroxide preferably range from 0.5 percent to 1.8 percent expressed as 100 percent H_2O_2 and need not be limited to 2 percent to 3 percent of 50 percent H_2O_2 (1 percent to 1.5 percent of 100 percent H_2O_2) as set forth above in an illustrative example of the invention, and when bleaching with 0.25 percent to 4 percent of 50 percent H_2O_2, based on the Oven Dried (O.D.) weight of pulp, the concentration is directly correlated to the consistency of the pulp system. Thus if a mill is bleaching with 0.25 percent of 50 percent H_2O_2 based on O.D. weight of pulp, then feeding must be carried out at very high concentration (25 percent of H_2O_2) to avoid greatly diluting the pulp consistency of the system which in turn reduces the efficiency of bleaching. Particularly valuable and efficient H_2O_2 concentration has been found to be in the range of 0.1 percent of 100 percent H_2O_2 to 1.75 percent of 100 percent H_2O_2 or 0.2 percent to 3.5 percent of 50 percent H_2O_2 per 100 parts of pulp. In addition, the invention is applicable not only to chemico-mechanical and mechanical pulps but also to cold soda pulp, unbleached sulfite pulp and neutral sulfite pulp. The temperature range for the bleaching can take place in the range of 90° F. to 180° F.

What is claimed is:

1. The method of bleaching wood pulp which consists essentially in adding to a pulp selected from the group consisting of mechanical, chemico-mechanical, cold soda, neutral sulfite and unbleached sulfite pulps, initially containing less than 10 percent solids, a sequestering agent to eliminate free metal ions in an amount of 1 to 2 pounds per 100 pounds of oven dried pulp, thickening the pulp to a solids concentration over 10 percent, feeding the thus treated pulp into a first mixer and introducing into the mixer a 2 to 25 percent by weight hydrogen peroxide solution at a pH of about 4.0 to 5.5 in an amount equivalent to about 0.5 to 2% expressed as 100% H_2O_2, thoroughly combining all ingredients in the mixer while heating with live steam to a temperature over 100° F. and in the range of 110° to 120° F., feeding the thus treated pulp to a second mixer while introducing thereinto an aqueous alkaline solution containing, calculated as NaOH, between about 1.25 and 1.8 parts of alkali per 100 parts of oven dried pulp with sufficient sodium silicate to effect buffering at pH 10.5 to 11 and maintaining the above temperature with steam, feeding the whole through a bleaching tower and retaining it there for not more than 90–120 minutes until bleached at about the same temperature, discharging the contents of the tower and adding SO_2 in an amount to neutralize the pulp and to reduce its pH to at least 6.

2. The method of bleaching wood pulp which consists essentially in adding to a pulp selected from the group consisting of mechanical, chemico-mechanical, cold soda, neutral sulfite and unbleached sulfite pulps, initially containing less than 10 percent solids, a sequestering agent to eliminate free metal ions in an amount of 1 to 2 pounds per 100 pounds of oven dried pulp, thickening the pulp to a solids concentration of about 14 to 15 percent by water removal, feeding the thus treated pulp into a first mixer and introducing into the mixer a 2 to 25 percent by weight hydrogen peroxide solution at a pH of about 4.0 to 5.5 in an amount equivalent to about 0.5 to 2% expressed as 100% H_2O_2, thoroughly combining all ingredients in the mixer while heating to about 90° F. to 180° F. with live steam, feeding the thus treated pulp to a second mixer while introducing thereinto an aqueous alkaline solution containing, calculated as NaOH, between about 1.25 and 1.8 parts of alkali per 100 parts of oven dried pulp with sufficient sodium silicate to effect buffering at pH 10.5 to 11 and maintaining the above temperature of 90° F. to 180° F. with steam, feeding the whole to a bleaching tower and maintaining it at about the same temperature for not more than 90–120 minutes until bleached, discharging the contents of the tower and adding SO_2 in an amount to neutralize the pulp and to reduce its pH to at least 6.

3. The method of bleaching wood pulp which consists essentially in adding to a pulp selected from the group consisting of mechanical, chemico-mechanical, cold soda, neutral sulfite and unbleached sulfite pulps, initially containing less than 10 percent solids, a sequestering agent to eliminate free metal ions in an amount of 1 to 2 pounds per 100 pounds of oven dried pulp, thickening the pulp to a solids concentration over 10 percent and in the neighborhood of 14 to 15 percent by water removal, feeding the thus treated pulp into a first mixer and introducing into the mixer 2 to 25 percent, by weight, H_2O_2 solution at a pH of about 4.0 to 5.5 in an amount equivalent to about 0.5 to 2% expressed as 100% H_2O_2, thoroughly combining all ingredients in the mixer while heating with live steam to a temperature over 100° F.

and in the range of 110° to 120° F., feeding the thus treated pulp to a second mixer while introducing thereinto an aqueous alkaline solution containing, calculated as NaOH, between about 1.25 and 1.8 parts of alkali per 100 parts of oven dried pulp with sufficient sodium silicate to effect buffering at pH 10.5 to 11 and maintaining the above temperature with steam, feeding the whole to a bleaching tower and retaining it there at about the same temperature for not more than 90–120 minutes until bleached, discharging the contents of the tower and adding SO_2 in an amount to neutralize the pulp and to reduce its pH to at least 6.

4. The method of claim 3 wherein the sequestering agent is tetrasodium ethylenediamine-tetraacetate.

5. The method of claim 3 wherein the sequestering agent is pentasodium diethylenetriamine-pentaacetate.

6. A method according to claim 3 in which the H_2O_2 solution has a concentration of 0.2 percent to 3.5 percent of 50 percent hydrogen peroxide per 100 parts of oven dried pulp.

7. The method of bleaching wood pulp which consists essentially in adding to mechanical wood pulp, initially containing less than 10% solids, a sequestering agent to eliminate free metal ions in an amount of 1 to 2 pounds per 100 pounds of oven dried pulp, thickening the pulp to a solids concentration over 10% and in the neighborhood of 14 to 15% by water removal, feeding the thus treated pulp into a first mixer and introducing into the mixer 2 to 3 parts per 100 parts of oven dried pulp of a 50% by weight H_2O_2 solution at a pH of about 4.0 to 5.5, thoroughly combining all ingredients in the

mixer while heating to about 110° to 120° F. with live steam, feeding the thus treated pulp to a second mixer while introducing thereinto an aqueous alkaline solution containing, calculated as NaOH, between about 1.25 and 1.8 parts of alkali per 100 parts of oven dried pulp with sufficient sodium silicate to effect buffering at pH 10.5 to 11 and maintaining the said 110° to 120° F. temperature with steam, feeding the whole to a bleaching tower and retaining it there for about 90 to 120 minutes at a temperature of 110° to 125° F., discharging the contents of the tower and adding SO_2 in an amount to neutralize the pulp and to reduce its pH to at least 6.

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DONALL H. SYLVESTER, *Primary Examiner.*

MORRIS O. WOLK, *Examiner.*

S. L. BASHORE, *Assistant Examiner.*