METHOD OF BLEACHING CELLULOSIC MATERIALS WITH HYDROGEN PEROXIDE

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This invention relates to a process for the bleaching of cellulosic materials, especially fibrous cellulosic materials, such as wood pulp and straw. It further relates to an improved process resulting in a high order of economy from hydrogen peroxide bleaching.

The primary object of bleaching cellulosic materials is to remove color-causing noncellulosic impurities from cellulosic materials or to modify them to facilitate their removal in a subsequent step. In bleaching ligneous cellulosic material, such as wood, it is customary to treat a pulp of the wood with chlorine, whereby much of the noncellulosic material is oxidized. A subsequent treatment with alkali such as sodium hydroxide, causes the dissolution of oxidized noncellulosic material and its removal as soluble, colored bodies in wash liquors. Subsequent steps of washing and bleaching then lighten the color of the cellulose. It is conventional to employ hypochlorite, chlorine dioxide and hydrogen peroxide in these subsequent steps to result in bleached cellulose.

The choice of steps employed in a bleaching sequence depends to a large degree upon the type of pulp employed and upon its prior treatment. Chemical wood pulp is often submitted to a sequence of bleaching steps which include a treatment with chlorine, a treatment with alkali (such as sodium hydroxide), a treatment with alkali metal hypochlorite (e.g., sodium hypochlorite), and one or more additional steps employing hydrogen peroxide or other oxidizing agent to produce a final high degree of whiteness.

Textile materials such as cotton are bleached in a sequence of steps although ordinarily a suitable textile sequence involves fewer steps than is employed in the bleaching of pulp. Thus, it is common to treat cotton and other cellulosic textile materials in an alkali scouring step prior to bleaching in a separate step with chemicals such as hydrogen peroxide.

Processes for bleaching cellulosic materials therefore involve a sequence of bleaching steps which include and often terminate with a treatment by hydrogen peroxide. When hydrogen peroxide is employed in a step of such a bleaching sequence, a large portion of the hydrogen peroxide does not produce any bleaching. Often as much as 30 or 40 percent, commonly 25 percent by weight of the hydrogen peroxide is discarded in the spent liquor because the concentration of hydrogen peroxide has become so low that it will no longer bleach rapidly.

Now it has been discovered that cellulosic material, such as wood pulp and other natural cellulosic materials, may be bleached by a sequence of steps utilizing hydrogen peroxide in one or more of such steps with substantial utilization of the hydrogen peroxide. It has been found that the rate at which hydrogen peroxide solution will bleach cellulosic materials may be accelerated to an economically attractive level when the hydrogen peroxide content is at low levels such as 1.0 percent by weight of the pulp or below. The addition of lower carbonyl acid anhydride in accordance herewith promotes the rate of reaction to consume all residual hydrogen peroxide in approximately 5 minutes. Thus, an aqueous slurry of cellulosic material containing hydrogen peroxide at very low levels such as 0.1 percent by weight of pulp or even less may be treated as here-in disclosed to consume all the hydrogen peroxide. Concentrations of hydrogen peroxide of less than 0.5 percent by weight of pulp are often economically utilized. These and other advantages will be apparent from the subsequent description of the instant invention.

In accordance with this invention cellulosic material, notably wood pulp, is bleached by procedures which include cooperative sequential treatment utilizing aqueous hydrogen peroxide solution and anhydride of organic carboxylic acid. This invention, in a principal embodiment, involves a two-stage procedure wherein organic carboxylic acid anhydride is added to a mixture of bleached pulp (or other cellulosic material) and bleaching liquors partially but incompletely depleted of hydrogen peroxide.

In the practice of an embodiment of this invention, a pulp of fibrous cellulosic materials is contacted with an aqueous solution containing alkaline aqueous hydrogen peroxide under conditions of temperature and time such that bleaching occurs and a substantial change in the light reflectance is observed. Then organic carboxylic acid, notably acetic anhydride, is added to the resulting pulp-hydrogen peroxide system and the bleaching continued.

Pulp suitably treated in accordance with the invention may be groundwood pulp. This is prepared by grinding wood of specified types with water in conventional pulp-making apparatus to obtain a slurry. The concentration of pulp (equivalent to weight percent) is expressed as percent consistency and has become the industry's standard as defined by the Technical Association of the Paper and Pulp Industries (TAPPI).

In the practice hereof any available commercial wood pulp may be employed although a typical wood pulp is composed of coniferous wood with a minor portion of aspen. Hardwood pulps such as those available in the south may also be employed although it is preferred to employ preliminary treatment for the prior removal of ligneous impurities. Other pulps useful in this invention may be prepared from bagasse and straw.

Pulp at a suitable consistency is treated hereinafter with an aqueous solution containing hydrogen peroxide to obtain a preliminary bleach. Alkali may be added either separately or with the hydrogen peroxide to provide a distinct alkaline reaction. Bleaching of the pulp begins on admixture with hydrogen peroxide. However, the rate of bleaching is slow at temperatures near 25° C. and impractical periods of time would be required to produce an appreciable brightening of the pulp. Hence it is preferred to bleach pulp with hydrogen peroxide at an elevated temperature at high as 100° C. In the practice hereof it is preferred that a temperature of 40 to 60° C., notably 60° C., is employed. When a temperature of 60° C. is employed, bleaching with hydrogen peroxide alone requires approximately 0.5 hour.

It has now been found that at the end of 0.5 hour, acetic anhydride (or other organic carboxylic acid anhydride) added to the pulp containing residual hydrogen peroxide results in the accelerated consumption of the residual hydrogen peroxide in a period of approximately 5 minutes at 50 to 60° C., while bleaching action from the residual peroxide is simultaneously obtained. Hydrogen peroxide for use herein may be provided as a dilute aqueous hydrogen peroxide or as 50 percent weight hydrogen peroxide as commercially available. Prepared in advance of utilization it has been found desirable to add sodium silicate solution and magnesium sulfate to the hydrogen peroxide to serve as bleach "stabilizers." Alternately the hydrogen peroxide may be added directly to the pulp for bleaching. Various stabilizers
such as sodium silicate or magnesium sulfate may likewise be added to the pulp at the commencement of the bleaching operation. The concentration of the chemicals employed in the practice hereof may be varied to suit conditions such as the degree of bleaching desired, the type of pulp employed, and the number of other steps employed in the bleaching sequence. The pulp concentration may be adjusted to 3 percent consistency. When bleached at such consistency it is preferred to adjust the sodium silicate to 5 percent by weight of the pulp solids. It is likewise preferred to adjust the magnesium sulfate concentration to 0.05 percent by weight of the pulp solids.

Initial hydrogen peroxide concentration may be adjusted from 1 to 10 percent by weight of the pulp solids, preferably 1.0 to 2 percent by weight. The pulp is then bleached by heating to a temperature selected within the bleaching range of 25 to 100°C, by way of illustration 60°C. At the end of 0.5 hour at 60°C, a sample of the pulp slurry is tested by conventional titration procedure and the residual hydrogen peroxide content is determined. Often one-half of the original peroxide remains. From this, the required molar equivalent of carboxylic acid anhydride is calculated, for example, acetic anhydride, and is added thereto. In approximately 5 minutes the bleaching is complete and the pulp is washed and processed in known manner.

Organic carboxylic acid anhydrides which are useful in this invention include anhydrides a monobasic or dibasic saturated carboxylic acid containing 2 to 8 carbon atoms. It is desired that the more reactive acid anhydrides are employed, for example the anhydrides of formic acid, acetic acid, propionic acid, n-butyric acid, isobutyric acid, malonic acid, succinic acid, and their mixed anhydrides. Preferred for economic reasons is acetic anhydride.

Bleaching is most advantageously carried out stepwise to obtain the benefits of bleaching with hydrogen peroxide alone in order to avoid too rapid bleaching and possible loss of hydrogen peroxide, followed by the addition of the acid anhydride at that point or stage at which the consumption of hydrogen peroxide and the desired bleaching action has slowed.

In place of hydrogen peroxide, inorganic peroxides which yield hydrogen peroxide on contact with water may also be employed, for example: alkali metal peroxydes, viz., sodium peroxide, potassium peroxide, and lithium peroxide and alkaline earth metal peroxides, viz., barium peroxide. Likewise, hydrogen peroxide yielding compounds such as percarbonates may be employed. It is preferred that the bleaching operation be carried out under conditions of alkali metal peroxides, viz., sodium peroxide, potassium peroxide, and lithium peroxide and alkaline earth metal peroxides, viz., barium peroxide. This is necessary prior to the addition of acid anhydride. However, after the addition of acid anhydride bleaching may be obtained under conditions of slightly acid reaction, such as a pH of 6. At very high pH values, viz., 11 to 12, extreme degradation of the cellulose material may result. Below about pH 5 bleaching action is impaired. Thus, it is preferred to bleach at pH values of 6.5 to 9. Often best results may be obtained at pH 8.

The time of bleaching is normally dependent upon the temperature. At 60°C for pre-bleaching about 30 minutes is required when the hydrogen peroxide concentration is 1 to 2 percent by weight of the pulp. An additional 5 minutes at this temperature and concentration will usually suffice after the addition of acid anhydride. Temperatures as high as 80°C may be employed although as the temperature approaches 100°C the hydrogen peroxide in the presence of the added acid anhydride is usually destroyed without producing a corresponding degree of bleaching. Lower temperatures, viz., 25°C fail to produce significant bleaching during the pre-bleaching stage. Thus, preferred temperatures for pre-bleaching are usually from 45 to 80°C for 10 to 45 minutes and after the addition of acid anhydride preferred tempera-
tures are somewhat lower, viz., 30 to 70°C for from 2 to 15 minutes. However, in commercial practice it is more convenient to operate both pre-bleaching and bleaching in the presence of acid anhydride at virtually the same temperature, viz., 50 to 65°C for about 30 minutes during pre-bleaching and about 3 to 10 minutes in the presence of added acid anhydride.

The pulp consistency is most conveniently adjusted to 3 percent but may be adjusted to as high as 30 percent or as low as 1 percent. High consistencies result in cellulose degradation due to high chemical concentration, while at one percent chemical inefficiency is often experienced. Therefore, it is preferred to operate at from 2 to 5 percent consistency and notably at 3 percent.

When extreme alkalinity is employed in pre-bleaching it is often desired to adjust the pH value. For this purpose mineral acids such as sulfuric, hydrochloric, and phosphoric may be employed. Organic acids such as acetic or an excess of acetic anhydride may also be used but are economically less desirable for pH adjustment.

The ratio of acid anhydride to hydrogen peroxide may be varied within wide limits without observable ill effects. When acetic anhydride is employed, the optimum results appear to result at a molar ratio of 1:1. Thus, the residual peroxide is determined by titration before adding acid anhydride. By way of illustration, a sample of partially bleached wood pulp in contact with residual bleaching liquors, on titration may be found to contain 0.68 percent by weight hydrogen peroxide. This requires adding sufficient acetic anhydride to give a solution initially having:

$$0.68 \times \frac{102}{94} = 7.04 \text{ percent}$$

by weight acetic anhydride on an equimolar basis. One-half of this amount may be employed at the penalty of an increase in the time required to consume the peroxide and finish the bleach. Large amounts, such as 5 percent by weight, approximately 2.5 moles, have no apparent ill effect except increased cost. Thus, it is preferred to employ the apparent optimum of approximately one mole per mole of hydrogen peroxide.

The invention may be better understood by reference to the following examples. It is understood that these examples are merely illustrative and are not to be construed as limiting.

**EXAMPLE I**

A sample of coniferous groundwood pulp was adjusted to 3 percent consistency and treated with 1.3 percent calcium chloride. A small pulp for 15 minutes at 25°C to insure pulp "freshness."

Reagents containing hydrogen peroxide were prepared with 41° Baumé aqueous sodium silicate and magnesium sulfate. These reagents were refrigerated until needed to minimize decomposition.

Samples of pulp were placed in containers with bleaching liquor and sodium hydroxide and adjusted to a 3 percent pulp consistency as defined by TAPPI (Technical Association of the Paper and Pulp Industry). Certain of the samples were then tested by titration to determine the residual hydrogen peroxide after a definite bleaching interval. A molecular equivalent amount of acetic anhydride based upon the residual hydrogen peroxide was added and the bleaching continued. The benefit obtained is indicated in Table I.

As a measure of bleaching it is customary to employ an instrument such as a Hunter reflectometer, which measures the percent of a given type of incident light which is reflected. The result is often expressed as percent light reflectance. However, a General Electric reflectance scale has recently become wide-spread and has to a degree replaced the Hunter reflectometer measurements. A pad of material is prepared by known procedures and is tested in the Hunter instrument for measuring light reflectance. The
data so obtained is converted into General Electric reflectance units.

<table>
<thead>
<tr>
<th>A. PRELIMINARY TREATMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Pulp Brightness, G.E. Units</td>
</tr>
<tr>
<td>Sodium Hydroxide, Percent by Weight</td>
</tr>
<tr>
<td>Temperature, °C</td>
</tr>
<tr>
<td>Bleaching Time, Hours</td>
</tr>
<tr>
<td>Bleached Pulp Brightness, G.E. Units</td>
</tr>
<tr>
<td>Residual Hydrogen Peroxide, Percent by Weight</td>
</tr>
</tbody>
</table>

B. BLEACHING CONTINUED WITH ADDITIONAL ACETIC ANHYDRIDE

<table>
<thead>
<tr>
<th>Continued Time, Hrs.</th>
<th>Residual H₂O₂, Percent</th>
<th>Brightness, G.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide Only (Control)</td>
<td>0.5</td>
<td>0.425</td>
</tr>
<tr>
<td>Hydrogen Peroxide and Anhydride (1.50 percent by weight)</td>
<td>0.08</td>
<td>0.0</td>
</tr>
</tbody>
</table>

EXAMPLE II

Example I was repeated employing 2.0 percent by weight sodium hydroxide and resulted in a preliminary bleached pulp having 67.0 brightness (G.E. units) with residual liquor containing 0.52 percent by weight hydrogen peroxide. Table II shows the bleaching obtained.

<table>
<thead>
<tr>
<th>Continued Time, Hrs.</th>
<th>Residual H₂O₂, Percent</th>
<th>Brightness, G.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide Only (Control)</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Hydrogen Peroxide and Acetic Anhydride (1.50 percent by weight)</td>
<td>0.08</td>
<td>0.0</td>
</tr>
</tbody>
</table>

EXAMPLE III

Example I was repeated employing 0.5 percent hydrogen peroxide, 0.75 percent sodium hydroxide by weight of pulp solids to give a preliminary bleached pulp having a brightness of 65.5 G.E. units and residual liquor containing 0.34 percent by weight hydrogen peroxide. The bleaching produced is as follows:

<table>
<thead>
<tr>
<th>Continued Time, Hrs.</th>
<th>Residual H₂O₂, Percent</th>
<th>Brightness, G.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide Only (Control)</td>
<td>0.5</td>
<td>0.20</td>
</tr>
<tr>
<td>Hydrogen Peroxide and Acetic Anhydride (1.50 percent by weight)</td>
<td>0.08</td>
<td>0.0</td>
</tr>
</tbody>
</table>

EXAMPLE IV

Example I was repeated employing 0.5 percent hydrogen peroxide, 2.0 percent sodium hydroxide by weight of the pulp solids at a bleaching temperature of 66°C. This resulted in a preliminary bleached pulp having a G.E. brightness of 65.0 units and residual liquor containing 0.225 percent hydrogen peroxide by weight of pulp. Addition of acetic anhydride resulted in the following:

<table>
<thead>
<tr>
<th>Continued Time, Hrs.</th>
<th>Residual H₂O₂, Percent</th>
<th>Brightness, G.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide Only (Control)</td>
<td>0.5</td>
<td>0.09</td>
</tr>
<tr>
<td>Hydrogen Peroxide and Acetic Anhydride (0.05 percent by weight)</td>
<td>0.08</td>
<td>0.0</td>
</tr>
</tbody>
</table>

EXAMPLE V

Example I was repeated employing 12 percent consistency pulp having a brightness of 61.1 G.E. units. After 1 hour from 1.5 percent only 0.23 percent hydrogen peroxide by weight of pulp remained. One-half of the calculated molecular equivalent of acetic anhydride was added and bleaching was continued for 0.084 hour at 70°C. The final brightness was 75.0 G.E. units.

The invention described herein is useful as a bleaching process for groundwood pulp bleaching. It is admirably suited to use as the second stage of a two-step procedure wherein the pulp is bleached with alkaline peroxide to result in partial bleaching and residual peroxide liquor containing from 0.2 to 1.0 percent hydrogen peroxide by weight of pulp which would usually be wasted. Low concentration levels of hydrogen peroxide, viz., below 0.2 percent by weight of pulp may be utilized but generally result in imperceptibly small bleaching improvement, hence residual concentrations above 0.2 percent by weight of pulp are preferred. Concentrations of residual hydrogen peroxide greater than about 1.5 percent by weight of pulp are still capable of producing moderately rapid bleaching without adding carboxylic acid anhydride. Hence, 0.2 to about 1.0 percent by weight of pulp is the preferred residual hydrogen peroxide concentration. The addition of acid anhydride permits unexpected additional bleaching in a very short time. Thus, greater economy of hydrogen peroxide is realized. Additional operations may be employed in combination with the procedure of this invention. It is preferred, however, in employing these other processes first as in the illustration of bleaching a hardwood pulp. Thus, steps as follows may be employed: chlorination; caustic extraction; hypochlorite bleaching; chlorine dioxide, hydrogen peroxide or additional hypochlorite bleaching followed by either a one-stage or a two-stage final operation in accordance herewith. Further, the invention may be applied to chemi-ground wood pulp, semi-chemical wood pulp, groundwood pulp or partially bleached pulp from separate operations.

Wood fibers such as straw, bagasse, hemp, sisal, bast, rambie, abaca, jute, flax, and linen may also be treated by the process herein.

Textile fibers of cellulosic nature, viz., cotton, linen, etc., may also be treated by the disclosed invention. Mixtures of woody fibers and cotton-like fibers such as those employed in rag paper manufacture are not precluded.

While the invention has been described with reference to the details of certain specific embodiments, it is not intended to limit the invention thereto except insofar as indicated in the following claims.

We claim:

1. A method of bleaching cellulosic material which comprises contacting said material with aqueous hydrogen peroxide solution to provide bleached material in contact with residual hydrogen peroxide and thereafter treating such bleached material still in contact with residual hydrogen peroxide with anhydride of 2 to 8 carbon carboxylic acid.

2. A method of bleaching cellulosic material which comprises contacting said material with aqueous hydrogen peroxide solution containing from 1 to 10 percent by weight hydrogen peroxide, consuming a portion but not a negligible fraction of hydrogen peroxide whereby to bleach said material, thereafter adding carboxylic acid anhydride to the solution of reduced hydrogen peroxide content in contact with said material and effecting further bleaching of the material.

3. In the method of bleaching cellulosic material by treatment with aqueous hydrogen peroxide solution, the improvement which comprises adding carboxylic acid anhydride to the hydrogen peroxide solution in contact with cellulosic material after the hydrogen peroxide content of said solution has been partially depleted by bleaching.
ing cellulosic material, and effecting additional bleaching therewith.

4. In the method of bleaching cellulosic material by treatment with aqueous hydrogen peroxide solution, the improvement which comprises accelerating the rate at which hydrogen peroxide solution containing less than 1.0 percent by weight hydrogen peroxide bleaches cellulosic material by adding to said solution carboxylic acid anhydride of 2 to 8 carbon atoms.

5. The method of claim 1 wherein from 0.5 to 2.5 moles of carboxylic acid anhydride per mole of residual hydrogen peroxide is employed.

6. The method of claim 1 wherein carboxylic acid anhydride is added to an aqueous hydrogen peroxide bath containing from 0.2 to 1.0 percent by weight of residual hydrogen peroxide.

7. The method of claim 1 wherein said cellulosic material is wood pulp.

8. The method of claim 1 wherein said carboxylic acid anhydride is acetic anhydride.

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