United States Patent

Lincoln et al.

[15] **3,645,840**

[45] **Feb. 29, 1972**

[54] METHOD FOR PEROXIDE BLEACHING OF PULP

[72] Inventors: **Robert M. Lincoln**, Moylan; **Joseph A. Meyers, III**, Springfield, both of Pa.

[73] Assignee: **Atlantic Richfield Company**, New York, N.Y.

[22] Filed: **Jan. 19, 1971**

[21] Appl. No.: **107,843**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 781,989, Dec. 6, 1968, abandoned.

[52] **U.S. Cl.** **162/78**, 8/111, 162/76

[51] **Int. Cl.** **D21c 3/00**

[58] **Field of Search** 162/72, 76, 78; 8/111, 111.5, 8/111.6

Primary Examiner—Howard R. Caine

Attorney—John J. McCormack and John D. Peterson

[57] **ABSTRACT**

Bleaching of ligneous cellulosic materials such as paper pulp by treating the pulp with a combination of tertiary butyl hydroperoxide and hydrogen peroxide as the bleaching agent.

4 Claims, No Drawings

METHOD FOR PEROXIDE BLEACHING OF PULP

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of our copending application Ser. No. 781,989, filed Dec. 6, 1968, entitled *METHOD FOR PEROXIDE BLEACHING OF PULP*, and now abandoned.

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

This invention relates to a method for producing ligneous cellulosic materials of improved brightness, in particular paper pulp by bleaching with tertiary butyl hydroperoxide in combination with hydrogen peroxide.

2. PRIOR ART

Hydrogen peroxide has been used advantageously in bleaching "high yield" pulps such as groundwood, despite its high cost since with careful use it can bleach without causing yield loss or without reducing the degree of polymerization of the cellulose. Hydrogen peroxide also has been used as a finishing bleach in draft paper manufacture after the noncellulosic components have been reduced by a series of steps including chlorination, alkaline washing, and chlorine dioxide bleaching.

The chemistry of hydrogen peroxide bleaching is incompletely understood, however, it is believed that the hydrogen peroxide in solution ionizes reversibly to form a hydrogen ion and a perhydroxyl ion, the latter is believed to be the active species in the bleaching reaction. Hydrogen peroxide can also decompose to release free oxygen. The oxygen released by this decomposition of hydrogen peroxide is said not to have any bleaching action but instead may actually be harmful by causing chain scission of the cellulosic molecules. Therefore, care must be exercised to prevent this reaction.

This hydrogen peroxide decomposition reaction occurs even at room temperatures and is rapid at higher temperatures or in the presence of catalytic materials such as metal ions.

In our copending application, Ser. No. 753,713, filed Aug. 19, 1968, entitled *METHOD FOR BLEACHING PULP* it was disclosed that an organic hydroperoxide such as tertiary butyl hydroperoxide, in particular, can be utilized for bleaching paper pulp instead of hydrogen peroxide. It was shown that the paper pulp can be bleached by replacing hydrogen peroxide with an equal amount of the tertiary butyl hydroperoxide and that the brightness increase obtained with the hydroperoxide was found to be the same as for the hydrogen peroxide. The advantage of using the tertiary butyl hydrogen peroxide is that such compound is quite stable and, in general, decomposes only at temperatures above about 100°-110° C. in the absence of reducing agents.

Various peracids in particular peracetic acid in conjunction with chlorine dioxide have also been proposed as bleaching agents. Peracetic acid, however, is extremely unstable and decomposes with explosive violence at about 110° C. and therefore must be handled with extreme caution even at low temperatures.

That tertiary butyl hydroperoxide can be utilized as a bleaching agent is completely unexpected in view of the wide differences in chemical reactivity among tertiary butyl hydroperoxide, hydrogen peroxide and the peracids. For example, olefins, in general, are converted smoothly and in good yields to the corresponding epoxides by peracids at low temperatures (0°-25° C.) while similar results are obtained with hydroperoxides only at higher temperatures (90°-120° C.) and only in the presence of a transition metal catalyst such as molybdenum. Hydrogen peroxide does not epoxidize olefins either in the presence or in the absence of catalysts.

Ketones are converted to esters and lactones by peracids while much poorer results are obtained with hydrogen peroxide and then only in the presence of a base as a catalyst. Hydroperoxides on the other hand do not react with ketones.

Base catalyzed hydrogen peroxide converts aromatic aldehydes and ketones having an amino or a hydroxyl group in the ortho or para position to the corresponding amino phenols or polyphenols but neither hydroperoxides nor peracids can be used in this reaction. These differences in chemical reactivity therefore render the use of tertiary butyl hydroperoxide as a bleaching agent to be completely unexpected.

Tertiary butyl hydroperoxide provides additional advantages over hydrogen peroxide and the peracids. It is stable in aqueous solutions and does not require stabilizing agents. It does not lose its bleaching strength in the presence of metallic ions such as Fe, Co, Ni, etc., ions whereas hydrogen peroxide for example must be stabilized and is most effective only with sequestering agents being present or alternatively by removing the metal ions from the pulp solution prior to bleaching.

Tertiary butyl hydroperoxide has an exceedingly important advantage over hydrogen peroxide or the peracids such as peracetic acid in that it is an excellent agent for preventing microbiological attack on the pulp. This feature is a unique and important advantage since molds or other microbiological growths on pulp follow through the process and finally degrade the quality of the finished paper.

The method of the present invention employs a combination of hydrogen peroxide and tertiary butyl hydroperoxide as the bleaching agents. While this method does not completely obviate the disadvantages of using hydrogen peroxide alone it does provide the advantages of using tertiary butyl hydroperoxide, i.e., economy and inhibition of microbiological growths. It also provides an additional advantage, namely, that a nonpolluting environment can be employed, i.e., the alkaline agent employed in conjunction with the bleaching agents may be sodium carbonate or sodium bicarbonate instead of the sodium silicate heretofore required with the hydrogen peroxide system. Sodium silicates are polluting agents and thus generally found their way into the waste water stream or otherwise required costly recovery methods.

The present method also provides an additional advantage, namely, it can be carried out at ambient temperatures. Heretofore, the hydrogen peroxide system had to be carried out at high temperatures for short times in order to minimize mold growths. The present method allows ambient temperature treatment giving the desired brightness improvement while completely inhibiting mold growth. Ambient temperature treatment is particularly desirable with hydrogen peroxide present since this lessens the attack on the cellulose fibers and provides a superior pulp for paper manufacture.

SUMMARY OF THE INVENTION

In accordance with this invention a combination of tertiary butyl hydroperoxide with hydrogen peroxide is utilized to bleach ligneous cellulosic materials such as pulp for paper manufacture.

It is an object of this invention therefore to provide an improved method for bleaching ligneous cellulosic materials.

It is another object of this invention to provide a method for bleaching ligneous cellulosic materials utilizing the combination of tertiary butyl hydroperoxide with hydrogen peroxide as the bleaching agent.

Other objects of this invention will be apparent from the description of the preferred embodiments which follows and from the claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of this invention is particularly adapted for the bleaching of cellulosic fibers and materials that are derived from lignin-containing materials by any of the processes that are generally used for fiber liberation.

The invention is particularly applicable to the bleaching of groundwood pulp, i.e., pulp containing large amounts of lignin. Heretofore approximately 80 percent of the hydrogen peroxide utilized in pulp bleaching has been for the bleaching of groundwood pulp, however, this invention is also applicable to treating any pulps which may be treated with hydrogen peroxide at some stage in their manufacture, for example, kraft pulp.

In recent years a method for the epoxidation of olefinic compounds has been developed utilizing an organic hydroperoxide as the oxidizing agent in a catalytic process. The large requirement for hydroperoxides for this process has led to the development of a convenient and economic process for producing organic hydroperoxides in particular tertiary butyl hydroperoxide by the noncatalytic oxidation of isobutane with molecular oxygen. This process has been known for a number of years and is now being developed commercially. Consequently, tertiary butyl hydroperoxide can be produced at a price much lower than that of hydrogen peroxide.

Since it has been found in accordance with this invention that tertiary butyl hydroperoxide can be combined with hydrogen peroxide to give brightness values greater than with hydrogen peroxide alone, this method has the additional advantage of permitting the use of tertiary butyl hydroperoxide in place of simply larger quantities of hydrogen peroxide.

The use of tertiary butyl hydroperoxide in combination with hydrogen peroxide therefore extends the range of brightness possible by a given dosage of hydrogen peroxide, and makes exact dosage of the hydrogen peroxide unnecessary. Exact dosage is normally required to prevent cellulose damage, but excess hydroperoxide can be used and recovered.

Although it is extremely difficult to demonstrate quantitatively, it is believed that another very important advantage of the hydrogen peroxide-tertiary butyl hydroperoxide combination of this invention lies in the milder action of the combination. Hydrogen peroxide alone is rapid, severe and indiscriminate in its attack, particularly since it is used at elevated temperatures to minimize mold growth, thus by limiting the amount of hydrogen peroxide employed and by allowing lower treating temperatures there are two realizable advantages one in prevention of yield loss and the second in improvement in pulp quality.

Hydrogen peroxide treatment is followed by a sulfite after-treatment in order to avoid color reversion due to active oxygen-containing compounds remaining in the pulp and to complete the decolorization of the color bodies to colorless compounds. Sodium hydrogen sulfite (sodium bisulfite) can be used as an after-treatment compound although other sulfites such as sulfur dioxide bubbled into the system also can be utilized. With the hydrogen peroxide-tertiary butyl hydroperoxide treatment, sulfite treatment can be omitted.

The amount of hydrogen peroxide utilized to treat the pulp is in the same range as that utilized by the industry when hydrogen peroxide is used as the sole bleaching agent. In general, amounts ranging between 0.1 weight percent to 5 weight percent of the dry pulp can be used although even larger amounts can be employed. Amounts in the range of from 0.5 to 2.0 are generally satisfactory when used in combination with the tertiary butyl hydroperoxide. The amount of tertiary butyl hydroperoxide may range between about 2 weight percent to 10 weight percent based on the weight of the dry pulp, with about 5 weight percent being generally satisfactory.

The amount of sulfite, for example, sodium hydrogen sulfite for the after-treatment can range between 1 weight percent and 6 weight percent, although this is not critical, and higher or lower amounts may be employed. Preferably an aqueous solution of about 10 percent concentration is employed and the amount used is about 10 percent concentration is employed and the amount used is sufficient to adjust the pH to the desired level, for example, a pH of 6.8 although this may be varied as experience dictates.

Sodium silicate is the recommended buffer for hydrogen peroxide bleaching according to the prior art and it is known that hydrogen peroxide is less effective in the absence of a buffer. It has also been found in the instant invention that it is preferable to employ a buffer in the bleaching step. Sodium silicate also can be employed in this invention, i.e., the ordinary commercial material known as "water glass." In general, the commercial sodium silicate wherein the SiO_2 to Na_2O ratio is from 1.6:1.0 to 2.4:1.0 is satisfactory and the amount of sodium silicate can vary between about 3 weight percent and 7 weight percent based on the weight of the dry pulp with 5 weight percent being quite suitable. Since silicates present pollution problems it is preferred in this invention to employ either sodium carbonate or sodium bicarbonate as the buffer since neither of these present any pollution problems. Between 3 and 7 weight percent are also suitable for these buffers.

It has also been found preferable to include a small quantity of sodium hydroxide. In general, the amount of sodium hydroxide is approximately one-half the weight of the buffer, i.e., in general, about 2.5 weight percent being satisfactory, although amounts ranging between 1 percent and 4 percent can be used. Sodium hydroxide can be completely eliminated, however, without loss in brightening improvement.

In order to demonstrate bleaching effectiveness of the combination of hydrogen peroxide with tertiary butyl hydroperoxide a number of runs were carried out to compare hydrogen peroxide alone with the combination of hydrogen peroxide and tertiary butyl hydroperoxide.

Laboratory tests were standardized and based on TAPPI Routine Control test methods. The pulp employed was a commercial groundwood. The pulp as received has a Photovolt Reflectance (brightness) of 70. It is well recognized in this art that an acceptable color improvement by hydrogen peroxide or similar competitive bleaching agents is 10 units, i.e., a Photovolt value of 80.

The test method consists of first conditioning the pulp. The pulp as received contains approximately 83 percent water. A slurry of this pulp in water was made by admixing 1 weight of pulp as received with 2 weights of water. This mixture was allowed to stand overnight and then mixed for 10 minutes with a wire beater and filtered in a Buchner funnel for 15 minutes using a rubber dam. The resulting cake is used as the stock for the bleaching test. The cake in general contains about 20 percent dry pulp. A sufficient amount of the stock prepared as described above contained in a polyethylene bag is admixed with aqueous hydrogen peroxide, aqueous sodium silicate or other buffer, aqueous sodium hydroxide (if used), an aqueous solution of tertiary butyl hydroperoxide and sufficient additional water to give a 10 percent consistency, i.e., 10 grams of dry pulp and 90 grams of total water. The hydrogen peroxide, buffer and tertiary butyl hydroperoxide were in amounts sufficient to give the weight concentrations based on the dry pulp as shown in the table in the Example. In each case the water is adsorbed by the pulp and there is little free liquid.

The polyethylene bag is kneaded to mix the pulp, bleaching solution and buffer and is then immersed in a water bath at 170° F. for one hour. On removal from the bath the after-treating agent is mixed by kneading and after 15 minutes the pulp is poured onto a Buchner funnel where the superficial liquid is removed through a filter paper. The after-treating agent in the runs in the Example was a 10 percent aqueous sodium hydrogen sulfite solution in an amount sufficient to adjust the pH to a value of 6.8.

After removal of the superficial liquid the pulp on the funnel is covered by a second piece of filter paper and placed between layers of felt. The pulp bed covered by the filter paper and felt is squeezed between rubber rollers and then dried in an oven at 110° C. for one hour with the filter paper covers in place. Following the oven drying step the amount of bleaching obtained is determined by measuring the reflectance by Model 610 Photovolt Reflectometer and comparing it with a hand sheet made by the same procedure without bleaching or after-treating solution.

The Photovolt Reflectometer for this purpose uses a blue filter and the brightness values thus obtained can be converted to TAPPI official General Electric brightness values. The Photovolt Reflectometer is adjusted so that a standard magnesium oxide block reads 100 percent reflectance.

In the runs which follow no values are shown for treating with tertiary butyl hydroperoxide alone, since it was found that under these test conditions that a brightness improvement of from only two to four points was obtained.

The runs in the following examples are provided to demonstrate the effectiveness of the combined hydrogen peroxide and tertiary butyl hydroperoxide treating as compared with either the hydrogen peroxide or hydroperoxide alone. These runs should not be construed, however, as limiting the invention solely to what is shown in the Examples.

EXAMPLE I

A series of runs were made on Poplar (hardwood) groundwood utilizing the procedure set forth above. The results of these tests are set forth in the Table together with the test conditions for each run. The amounts set forth are weight percent based on the weight of dry pulp.

TABLE

Percent H_2O_2	Percent TBHP*	Percent sodium silicate	Percent NaOH	Brightness
0	0	0	0	70
0.25	0	5	1.3	76
0.25	5	5	1.3	79
0.50	0	5	2.7	79
0.50	5	5	2.7	82
0.50	10	5	2.7	83
0.75	0	5	2.5	82
0.75	2	5	2.5	84
0.75	5	5	2.5	85
1.00	0	5	2.5	84
1.00	5	5	2.7	87
2.00	0	5	2.5	87
2.00	10	5	2.5	89
3.00	0	5	2.5	89
0.50	0	0	4.0	74
0.50	6.7	0	4.0	84
0.50	13.3	0	4.0	85

*TBHP—tertiary butyl hydroperoxide.

These results show that the same brightness improvement can be obtained by using only 0.25 weight percent H_2O_2 and 5 percent tertiary butyl hydroperoxide as can be obtained with twice the amount of H_2O_2 alone. Similarly, at a brightness level of 87, 1 weight percent H_2O_2 with 5 weight percent tertiary butyl hydroperoxide can be used and is equivalent to twice the weight percent H_2O_2, i.e., 2 weight percent. At a brightness level of 89 which is 19 points above the starting level of 70 for the unbleached pulp, a 50 percent increase in H_2O_2 is required to be equivalent to 2 weight percent H_2O_2 together with 10 weight percent tertiary butyl hydroperoxide. Accordingly, these results show the usefulness of the method of this invention.

The following Examples are provided for the additional purpose of demonstrating the ability of tertiary butyl hydroperoxide to improve the hydrogen peroxide bleaching of groundwood (mechanical) pulps by (a) replacing the prior art polluting alkali silicate with nonpolluting alkali carbonate or bicarbonate and (b) allowing storage-bleaching at ambient temperatures with the hydrogen peroxide-tertiary butyl hydroperoxide agents, wherein the tertiary butyl hydroperoxide also prevents mold formation.

EXAMPLE II

Into a polyethylene bag was weighed 18.8 grams (3.0 grams, oven dried) of white spruce refiners groundwood, 1.0 grams of 10 weight percent hydrogen peroxide, (3.3 weight percent of dry pulp), 5.0 grams of 10 percent sodium carbonate (aq.) and 15.0 grams of distilled water. The pulp was manually mixed thoroughly with the aqueous additives to give a pulp of 7.5 percent consistency which showed no free liquid but from which liquid could be easily squeezed.

In a parallel run the above conditions were repeated and in addition, 0.3 gram of tertiary butyl hydroperoxide was included. After standing at room temperature for 10 days, the pulp without tertiary butyl hydroperoxide had darkened, as compared to untreated pulp. The darkening was due to mold formation which was seen in discrete colonies which in 3 weeks had permeated the entire pulp.

The bag containing tertiary butyl hydroperoxide after 5 days at room temperature was free of mold and had brightened as shown by Photovolt readings on handsheets from the untreated reading of 75 to 83.

Observation of the pulps after 2 months showed greatly increasing mold formation and darkening in the pulp containing no tertiary butyl hydroperoxide, the tertiary butyl hydroperoxide treated sample was mold free and had brightened considerably over the handsheet which read 83 after 5 days.

EXAMPLE III

The procedure of Example II was repeated using 0.3 gram of sodium bicarbonate in place of the 0.15 gram of sodium carbonate. As before, parallel runs were made (a) without tertiary butyl hydroperoxide and (b) with 0.3 gram tertiary butyl hydroperoxide. The results after 5 days at room temperature were, to the eye, the same as the sodium carbonate pulps of Example II. A Photovolt reading on a handsheet after 5 days read 82 for the tertiary butyl hydroperoxide treated pulp. The pulp with no tertiary butyl hydroperoxide added was darker, after 5 days at room temperature, than the starting pulp and mold colonies were easily seen. After 2 months the tertiary butyl hydroperoxide treated sample had continued to brighten while the pulp with no tertiary butyl hydroperoxide present was uniformly moldy. Little difference between sodium carbonate and sodium bicarbonate is seen with respect to mold formation.

EXAMPLE IV

The procedure of Examples II and III was repeated using 0.30 gram of 40°-42° Baume sodium silicate in place of sodium carbonate or bicarbonate.

The results differed from those of Example II and Example III, in that, silicate and hydrogen peroxide gave brightening at room temperature in the absence of tertiary butyl hydroperoxide. However, the brightness increase was negated by formation of mold colonies, so that, after 5 days some areas of the pulp were as bright as the tertiary butyl hydroperoxide treated pulp, but, overall, the mold colonies caused an overall brightness inferior to the tertiary butyl hydroperoxide treated sample. After 2 months, mold formation was extensive in the silicate-hydrogen peroxide treated pulp while the tertiary butyl hydroperoxide (0.3 gram) containing pulp was mold free.

Photovolt readings on the tertiary butyl hydroperoxide treated hydrogen peroxide, silicate bleached pulp after 5 days were 85. This compares with Photovolt readings of 75 for the unbleached white spruce groundwood; 82 for hydrogen peroxide, sodium bicarbonate, tertiary butyl hydroperoxide treated pulp and 83 for hydrogen peroxide, sodium carbonate, tertiary butyl hydroperoxide, treated pulp.

The brightness obtainable by the methods of Examples II and III can be increased by the usual above-discussed sulfite after-treatment. Sodium hydroxide, however, is not employed with the sodium carbonate or bicarbonate.

The importance of the foregoing Examples is emphasized by reference to TAPPI Monograph No. 27 "Bleaching of Pulp" 1963, wherein on page 190 it is stated that mechanical pulps are preferably bleached with hydrogen peroxide immediately after grinding, however when mold and spoilage of pulp is absent storage for 6 months or more is practical. On page 191 of the monograph it is pointed out that certain bacteria inherently present in the wood, reduce hydrogen peroxide efficiency by producing "catalase" which greatly accelerates hydrogen peroxide decomposition. Heretofore the bacteria were controlled by heat, chlorinating agents and bactericides usually heavy metal compounds such as mercurial compounds all of which are polluting materials.

In the instant process any unreduced tertiary butyl hydroperoxide is recovered by separation of its reduction product, tertiary butyl alcohol. The tertiary butyl alcohol is easily separated from the water by distillation in the form of its

azeotrope with water, and is readily burned in this form to produce carbon dioxide and water which step also produces useful process heat. Thus, the instant method is completely nonpolluting either with respect to air pollution or with respect to water pollution.

We claim:

1. A nonpolluting method of bleaching ligneous cellulosic fibers which comprises contacting the cellulosic fibers with an aqueous solution of hydrogen peroxide and tertiary butyl hydroperoxide in the presence of a buffer, said hydrogen peroxide ranging in an amount of from about 0.1 weight percent to 5.0 weight percent based on the weight of the dry cellulosic fibers, said hydroperoxide ranging in an amount from 2 weight percent to 10 weight percent based on the weight of the dry cellulosic fibers and said buffering agent being sodium carbonate or sodium bicarbonate and ranging from 3 weight percent to 7 weight percent based on the weight of the dry cellulosic fibers.

2. The method according to claim 1, wherein the cellulosic fibers which have been treated with hydrogen peroxide, tertiary butyl hydroperoxide and buffer are treated with a sulfite compound said sulfite compound ranging in an amount from about 1 weight percent to 6 weight percent based on the weight of the dry cellulosic fibers.

3. The method according to claim 1, wherein the said buffer is sodium carbonate.

4. The method according to claim 1, wherein said buffer is sodium bicarbonate.

* * * * *