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[54] **METHOD FOR BLEACHING GROUNDWOOD PULP WITH TERTIARY BUTYL HYDROPEROXIDE**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 753,713, Aug. 19, 1968, abandoned.

[52] **U.S. Cl.** **162/71**, 8/111, 162/78, 162/84

[51] **Int. Cl.**.....**D21c 9/16**

[58] **Field of Search** 162/78, 76, 72; 8/111, 111.5, 8/111.6; 162/84, 71

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[57] **ABSTRACT**

Bleaching of ligneous cellulosic materials such as groundwood pulp by treating the pulp with an aqueous solution of tertiary butyl hydroperoxide and a buffering agent and thereafter contacting the pulp with a sulfite compound.

6 Claims, No Drawings

METHOD FOR BLEACHING GROUNDWOOD PULP WITH TERTIARY BUTYL HYDROPEROXIDE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of our co-pending application Ser. No. 753,713, filed Aug. 19, 1968, entitled METHOD FOR BLEACHING PULP, now abandoned.

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

This invention relates to a method for preparing ligneous cellulosic materials of improved brightness, in particular, paper pulp by bleaching with tertiary butyl hydroperoxide, and in a particular embodiment, after-treating with a sulfite compound.

2. PRIOR ART

The bleaching of paper pulp utilizing chlorine-containing compounds such as chlorine dioxide and the hypochlorites, has been practiced for a great number of years. Although the use of hydrogen peroxide for bleaching pulp has been more recent, it has been assuming an increasingly important role especially for bleaching high-yield pulps and for a finishing bleach for kraft pulps.

Hydrogen peroxide is used advantageously in bleaching "high yield" pulps such as groundwood, despite its high cost because with careful use it can bleach without causing yield losses or without reducing the degree of polymerization of the cellulose. Hydrogen peroxide is also used as a finishing bleach in kraft paper manufacture after the non-cellulosic 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 perhydroxyl ion 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 temperature and is rapid at higher temperatures or in the presence of catalytic materials such as metal ions. Tertiary butyl hydroperoxide decomposes only very slightly at temperatures above about 100° to 110° C. in the absence of reducing agents and thus is far more stable.

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 at low temperatures.

It now has been found that paper pulp can be bleached by replacing hydrogen peroxide with an equal amount of the more stable tertiary butyl hydroperoxide. The brightness increase obtained either by hydrogen peroxide or by tertiary butyl hydroperoxide has been found to be the same. It will be obvious, therefore, that since tertiary butyl hydroperoxide is available at a much more favorable price than the same weight of hydrogen peroxide, there is a valuable saving in using the hydroperoxide.

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.

Finally tertiary butyl hydroperoxide provides 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.

SUMMARY OF THE INVENTION

In accordance with this invention tertiary butyl hydroperoxide is utilized to bleach ligneous cellulosic materials such as paper pulp.

In a specific embodiment of the invention the bleaching agent is combined with a mild buffering agent such as sodium carbonate, sodium bicarbonate or the combination of sodium tripolyphosphate and a surfactant.

In a further specific embodiment of the invention the hydroperoxide bleaching step is followed by an after-treatment step with sodium sulfite, sodium bisulfite or the like.

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

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

It is another object of this invention to provide a method for bleaching ligneous cellulosic materials utilizing tertiary butyl hydroperoxide in combination with a mild buffering agent.

It is another object of this invention to provide a method for bleaching ligneous cellulosic materials utilizing tertiary butyl hydroperoxide followed by treatment with a sulfite.

Other objects of this invention will be apparent from the description of the preferred embodiments 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 per cent 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 are 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 and since equal weights of hydrogen peroxide and tertiary butyl hydroperoxide give equally good bleaching there is a considerable advantage for utilizing the hydroperoxide.

As has been pointed out organic hydroperoxides have the additional advantage of having greater stability as compared with hydrogen peroxide. Hydrogen peroxide, unless special precautions are followed as has been described, decomposes to give water and oxygen which is not suitable for bleaching. Such precautions are unnecessary with organic hydroperoxides since they decompose only at temperatures above 90° C.

It has been found that it is desirable in many instances to follow the tertiary butyl hydroperoxide treatment with an after-treat consisting of a sulfite 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. Sulfite compounds which can be used include Na_2SO_3, sodium bisulfite or sodium hydrogen sulfite, $NaHSO_3$, or sulfites produced in situ by bubbling sulfur dioxide into the alkaline solution. These are the preferred after-treatment materials.

In a particularly preferred embodiment of the invention a mild buffering agent such as sodium carbonate, sodium bicarbonate or the combination of sodium tripolyphosphate with a surfactant is combined with the tertiary butyl hydroperoxide in the bleaching step. Anionic surfactants are particularly preferred, the most preferred materials being the sodium alkylbenzene sulfonates. Particularly preferred are the linear alkylbenzene sulfonates wherein the alkyl group contains from about 11 to 14 carbon atoms with an average of about 12 carbon atoms since these materials are biodegradable. Although the tripolyphosphate-surfactant combination gives excellent results, whenever pollution is a problem, the carbonate or bicarbonate can be used equally well. None of these are in any way bleaching agents, but enhance the bleaching ability of the tertiary butyl hydroperoxide to an unexpected extent.

The amount of tertiary butyl hydroperoxide utilized to treat the pulp is in the same range as that utilized by the industry for hydrogen peroxide treating. In general, amounts ranging between 0.1 weight per cent to 2 weight per cent based on the weight of dry pulp can be used, although larger amounts also can be employed. The amount of sulfite, for example, sodium bisulfite for the after-treatment may range between 1 per cent and 6 per cent although this is not critical and lower or higher amounts may be employed. If SO_2 is employed an equivalent amount is used.

Sodium silicate is the recommended buffer for hydrogen peroxide bleaching and it is known that hydrogen peroxide is less effective in the absence of a buffer. It was found, however, that tertiary butyl hydroperoxide requires no strong alkali. This is desirable since the possibility of cellulosic breakdown which can occur under alkaline conditions is completely avoided.

In order to determine the bleaching effectiveness of tertiary butyl hydroperoxide as compared with hydrogen peroxide, tertiary butyl hydroperoxide as a bleaching agent was compared directly with hydrogen peroxide. Laboratory tests were standardized and based on TAPPI Routine Control test methods. The pulp employed was a commercial balsam plus pine groundwood. The pulp as received has a photovolt reflectance (brightness) of 65. 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 75. Since such an improvement is difficult to achieve under the most carefully controlled conditions, improvements in excess of 10 units are very unusual and are deemed extremely difficult to obtain.

The test method consists of first conditioning the pulp. The pulp as received contains approximately 50 per cent water. A slurry of this pulp in 9 weights of water is allowed to stand overnight, 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 stock for the bleaching test. The cake, in general, contains about 20 to 25 per cent dry pulp.

A sufficient amount of the stock prepared as described above is mixed with water in a polyethylene

bag to give a 10 per cent consistancy, i.e., 10 grams of dry pulp and 90 grams of total water. Under these conditions most of the water is absorbed by the pulp and there is little free liquid. The bleaching agent and buffer, if any, is added in an aqueous solution (generally about a 1.0 weight per cent solution of the bleaching agent) in an amount such that the desired quantity based on dry pulp of the bleaching agent and buffer is added to the pulp solution in the bag.

The bag is kneaded to mix the pulp and bleach solution and is then immersed in a water bath at 170° F. for one hour. On removal from the bath the sulfite after-treat 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.

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 pad covered by the filter paper and felt is squeezed between rubber rollers and then hung in an air current to air dry for 12 to 16 hours with the filter paper covers in place.

Following air drying the hand sheet is dried in an oven at 110° C. for one hour. Following the oven drying step the amount of bleaching obtained is determined by measuring the reflectance by a Model 610 Photovolt reflectometer and comparing it with a hand sheet made by the same procedure without bleaching or after-treat solution.

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

The following examples are provided to demonstrate specific aspects of the instant invention and to demonstrate its utility for the bleaching of paper pulp. These examples should not be construed as limiting the invention solely to the illustrations contained therein.

EXAMPLE I

A series of runs were made utilizing the procedure set forth above. The results of these tests are set forth in the Table which follows.

TABLE

Run No.	Bleach (wt. percent of dry pulp)	Buffer (wt. percent of dry pulp)	After-treat (wt. percent dry pulp)	Photovolt reflectometer, percent
1	None	None	None	65
2	0.5 H_2O_2	2.5 sodium silicate	1.5 $NaHSO_3$	66
3	1.0 H_2O_2	5.0 sodium silicate	3.0 $NaHSO_3$	71
4	2.0 H_2O_2	10.0 sodium silicate	6.0 $NaHSO_3$	74
5	0.5 TBHP [2]	None	1.5 $NaHSO_3$	73
6	1.0 TBHP	do	3.0 $NaHSO_3$	75
7	2.0 TBHP	do	6.0 $NaHSO_3$	75
8	1.0 H_2O_2	1.0 STPP [3] plus 1.0 Det.[4]	2.0 $NaHSO_3$	75
9	2.0 H_2O_2	2.0 STPP [3] plus 1.0 Det.[4]	2.0 $NaHSO_3$	77
10	1.0 TBHP	1.0 STPP [3] plus 1.0 Det.[4]	2.0 $NaHSO_3$	76
11	2.0 TBHP	2.0 STPP [3] plus 1.0 Det.[4]	2.0 $NaHSO_3$	77
12	None	None	2.0 $NaHSO_3$	71
13	do	do	4.0 $NaHSO_3$	71

[1] Photovolt reflectance, blue filter, MgO=100%.
[2] TBHP=tertiary butyl hydroperoxide.
[3] STPP=sodium tripolyphosphate.
[4] Det.=detergent (linear alkylbenzene sulfonate sodium salt, alkyl group 11 to 14 carbon atoms average, approximately 12 carbon atoms).

These data demonstrate that the the tertiary butyl hydroperoxide without silicate buffering gives superior bleaching results compared to hydrogen peroxide utilizing sodium silicate buffering, compare runs **2**, **3** and **4** with runs **5**, **6**, and **7**. The data also show that tertiary butyl hydroperoxide gives equally good bleaching when a buffering agent such as sodium tripolyphosphate and an alkyl benzene sulfonate is used, as compared with silicate buffered hydrogen peroxide, compare runs 8 and 9 with runs 10 and 11. Runs 12 and 13 show that the sodium bisulfite alone does not give the required improvement in brightness.

The data also show that a wide range of amounts of bleach, buffer and after-treating agent may be employed and that, in general, slightly better results are obtained with the larger quantities, although it will be recognized, of course, in accordance with well-known principles in the art that excessive amounts of bleaching agent should not be used. Tertiary butyl hydroperoxide, however, if used in excess of that required can be recovered for re-use while hydrogen peroxide or the peracids cannot be recovered.

Amounts of bleaching agent ranging between 0.1 weight per cent and 5 weight per cent based on the dry pulp are satisfactory and amounts of buffering agent, if used, can range between 0.5 and 10.0 per cent.

EXAMPLE II

Another series of bleaching runs were carried out in a similar manner as that employed in Example I except that sodium carbonate and sodium bicarbonate, respectively, were used as the buffering agents in combination with the tertiary butyl hydroperoxide bleaching agent in amounts ranging between 3.0 and 10.0 per cent by weight based on the weight of the dry pulp. Equally good brightening of the pulp was obtained as in the comparable runs of Example I.

In addition it has been observed that pulps bleached with tertiary butyl hydroperoxide upon standing show no tendency to discolor due to microbiological attack whereas pulps bleached with hydrogen peroxide, for example, become discolored because of such attacks by microorganisms.

We claim:

1. A method of bleaching lignin-containing groundwood pulp which comprises contacting said lignin-containing groundwood pulp with an aqueous solution consisting essentially of tertiary butyl hydroperoxide and a buffering agent selected from the group consisting of sodium carbonate, sodium bicarbonate, and the combination of sodium tripolyphosphate with a surfactant and thereafter contacting with a sulfite compound the lignin-containing groundwood pulp which has been contacted with the aqueous tertiary butyl hydroperoxide solution and buffering agent, said sulfite compound being in an amount sufficient to avoid color reversion.

2. The method according to Claim **1**, wherein said buffer-ing agent is sodium carbonate.

3. The method according to Claim **1**, wherein said buffer-ing agent is sodium bicarbonate.

4. The method according to Claim **1**, wherein said buffer-ing agent is sodium tripolyphosphate and a surfactant.

5. The method according to Claim **4**, wherein said surfactant is a linear alkylbenzene sulfonate wherein the alkyl group contains from 11 to 14 carbon atoms.

6. The method according to claim 1, wherein said sulfite compound is sodium sulfite or sodium bisulfite.

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