

1

2

3,707,438

**METHOD FOR THE BRIGHTENING OF
KRAFT PULP WITH TERTIARY BUTYL
HYDROPEROXIDE**

Robert M. Lincoln, Moylan, and Joseph A. Meyers III,
Springfield, Pa., assignors to Atlantic Richfield Com-
pany, Philadelphia, Pa.

No Drawing. Filed Sept. 15, 1970, Ser. No. 72,491

Int. Cl. D21c 9/16

U.S. Cl. 162—78

9 Claims

ABSTRACT OF THE DISCLOSURE

Method for replacing one or more of the chlorine or chlorine-compound bleaching steps of kraft pulp by the use of tertiary butyl hydroperoxide as a brightening agent in an alkaline medium, in particular aqueous sodium hydroxide or sodium carbonate. The amount of tertiary butyl hydroperoxide and alkaline medium required depends upon the extent of the prior bleaching of the kraft pulp.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a method for replacing one or more of the conventional chlorine bleaching steps of kraft pulp by the use of tertiary butyl hydroperoxide as a brightening agent in aqueous alkaline medium such as aqueous sodium hydroxide or sodium carbonate.

Prior art

Kraft brown stock, as obtained from the pulping process, requires extensive treatment with chlorine and chlorine-compounds in order to obtain a bleached and brightened pulp.

A large number of paper mills are designed to carry out this treatment in four stages. The first stage normally consists of treating with chlorine and the second stage, which follows, is an extraction with aqueous sodium hydroxide, these stages being designated C and E, respectively. Following the extraction stage the pulp is treated with hypochlorite, the H stage; the final brightness is obtained by treating with chlorine dioxide, the D stage. This four stage sequence, CEHD, gives kraft pulps having a G.E. brightness of 86 to 87. In order to obtain higher brightness levels numerous five stage processes have also been designed and used, for example, CEHHD, CEHDH, CEHED, CHDED and CEDED, wherein the letters refer to the same stages as described in the four stage sequence.

Six and eight stage bleaching processes are also used, for example, CEHDED, CHEDED, and CEHCHDED.

The primary reason for employing various sequences such as those described is to obtain the maximum amount of bleaching or brightness with minimum amount of chemical utilization and chemical cost. Another important reason for employing such sequences is to minimize the pulp yield loss since in obtaining bleaching by the use of these chlorine compounds some lowering of yields results by formation of water-soluble chlorinated compounds of cellulose and hemi-cellulose.

These prior art methods, however, are subject to many disadvantages. The most important are:

All of the sequences employ chlorine or chlorine-compounds which give both serious waste water and air pollution problems.

The compounds employed are expensive and thus must be used in exactly the optimum amounts in order to minimize the chemical cost and to avoid over-bleaching with attendant color and yield loss.

All of the sequences described cause some breakdown of cellulose with the consequent pulp yield loss.

The use of the hypochlorite stage causes some damage to the cellulose with consequent loss in strength and color stability, thus sequences were developed which obviate the use of hypochlorite entirely by the substitution of chlorine dioxide, i.e. additional D stages, but these also were more expensive.

Chlorine and chlorine dioxide are highly toxic and hazardous compounds, chlorine dioxide being highly explosive. All contact with the skin or with their vapors by employees using them must be avoided and this requires expensive and special precautions; and in addition, since they are so highly corrosive, special and expensive stainless steels must be employed in the equipment. Chlorine dioxide, in particular, is difficult to handle since gas phases containing more than 10 percent ClO₂ must be avoided and since water solubility is only 0.3 percent constant control and metering must be employed.

The method of the present invention obviates all of these difficulties.

The present method completely avoids the pollution problems associated with the prior art method which fact is of exceedingly great importance since the public and many governmental agencies are now greatly concerned with these types of pollution and are requiring either stringent curbing or their entire elimination.

The cost of the reagents for the instant process is either no greater or less than the chemical cost of the prior art chlorine bleaching compounds, and thus it is not as necessary to employ exactly optimum amounts of such reagents. In addition, critical amounts are not required to avoid color reversion as with the prior art processes. If an excess is used, it can be recovered and recycled.

The method of the instant invention provides brightness increase comparable to that of the prior art methods without delignification so that there is no pulp yield loss.

The present invention is completely flexible, that is it can be substituted for any one or all of the prior art stages, and thus is particularly suitable for replacing chlorine dioxide and obviating of the necessity of using two or more chlorine dioxide stages to replace hypochlorite and obtain final maximum brightness.

Finally, the tertiary butyl hydroperoxide requires only ordinary precautions in handling, is highly stable having none of the hazardous and toxic characteristics of chlorine or chlorine dioxide. Likewise, it is not as corrosive and ordinary stainless steels can be used in fabricating the equipment.

SUMMARY OF THE INVENTION

In accordance with the instant invention kraft pulps either as obtained in the form of the brown stock from the pulping stage of manufacture, or as obtained from any of the stages of conventional bleaching are treated with a mixture of tertiary butyl hydroperoxide and an alkaline compound such as sodium hydroxide or sodium carbonate in aqueous solution to provide a brightened pulp having a G.E. brightness equal to or greater than that obtained by the conventional prior art methods which have been described. The invention is applicable to both hard wood and soft wood types of pulps, and in a particular important embodiment of the invention, the alkaline tertiary butyl hydroperoxide treatment is used to replace conventional chlorine dioxide treatment.

It is an object of this invention, therefore, to provide an improved method for brightening kraft type pulps.

It is another object of this invention to provide a method for brightening kraft pulps which obviates the pollution problems of the prior art bleaching methods.

3

It is another object of this invention to provide a method for the brightening of kraft pulps which obviates the use of toxic and hazardous compounds.

It is another object of this invention to replace one or more of the prior art bleaching stages of kraft pulps by treatment with an aqueous solution of tertiary butyl hydroperoxide and an alkaline compound such as sodium hydroxide or sodium carbonate.

It is another object of this invention to provide a method for the use of an aqueous alkaline tertiary butyl hydroperoxide solution to replace chlorine dioxide in the brightening of kraft pulps.

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

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of this invention is applicable either to kraft pulp made from hard woods (angiosperms) or soft woods (gymnosperms). The method of this invention can be employed with kraft pulp as it is obtained directly from the pulping processes in the form of brown stock or after any one of the conventional bleaching stages, such as the chlorination stage (C), after the chlorination and extraction stages (CE), or after the hypochlorite stage (CEH). In the latter embodiment the brightening method of this invention replaces the chlorine dioxide or D stage of the kraft process. This constitutes a particularly preferred embodiment of the invention. In those mills wherein more than four stages of bleaching are employed and wherein the last three stages are DED stages, the method of this invention is also particularly applicable in replacing the two chlorine dioxide stages and extraction stage.

The method can be carried out on pulps having the consistency, normally associated with kraft pulps, i.e. those ranging from 12 to 20 percent, or lower or higher. Consistency refers to the weight percent of dry pulp in the bleaching or brightening liquor. Ordinarily, the consistency is based on air dried pulp weight, however, in the data in this application consistency is based on oven dried pulp weight.

The brightening method of this invention can be carried out at temperatures in the range of from ambient temperatures, 20° to 25° C., or below, to temperatures of 100° C. Temperatures in the range of from 70° C. to 85° C. are preferred in order to provide a shorter reaction time without reaching the temperature at which the hydroperoxide starts to decompose and vaporize, thereby reducing its effectiveness. Since the brightening reaction is dependent upon the temperature it may take up to two weeks at room temperature to obtain the same degree of brightening that can be obtained from as little as 15 minutes at 85° to 100° C. In general, at the preferred temperature range of from 70° C. to 85° C. times in the range of from 3 hours at the lower limit to ½ hour at the upper are preferred.

The brightening step is ordinarily carried out at atmospheric pressures although pressures above atmospheric, for example, up to 50 p.s.i.g. may be used if desired or subsatmospheric pressures may be used, for example, a few pounds below atmospheric pressure.

The weight percent based on the dry pulp of tertiary butyl hydroperoxide in the brightening liquor can range from about 0.5 to 50, however, from 20 to 40 weight percent based on the dry pulp is a more preferred range for both hard and soft wood pulps and when applied to brown stock or after the chlorination or chlorination and extraction stages. When applied to pulps in which the chlorine dioxide stage is being replaced, from 5 to 20 weight percent based on the dry pulp of tertiary butyl hydroperoxide in the brightening liquor is sufficient and some improvement is obtained even with from 0.5 to 2.5

4

percent. The brightening liquor can have a concentration of from about 5 to 20 weight percent tertiary butyl hydroperoxide although this is a matter of convenience and higher or lower concentrations can be employed.

The amount of alkaline compound employed depends upon the quantity of tertiary butyl hydroperoxide employed and also upon the pH desired. In general, sufficient alkaline compound, i.e. sodium hydroxide or sodium carbonate should be used such that the pH ranges from 8 to 10.5 with a preferred range being from about 9 to 10.5.

In general, in order to attain a pH of about 10.5, it is necessary to utilize a weight of sodium hydroxide amounting to about 40 percent of the weight of tertiary butyl hydroperoxide. The exact amount of alkaline compound, however, can be adjusted to attain or to maintain the pH at the desired level by making the necessary additions from time to time.

The method of this invention can also be carried out in more than one stage, for example, the pulp can be treated in a first stage and the brightening solution is drained from the pulp. The pulp is then treated with the solution to which tertiary butyl hydroperoxide and the alkaline compound have been added to bring the solution to the desired concentration. The addition of the water and brightening mixture also is useful in maintaining the desired consistency of the pulp.

The following examples are provided in order to provide a better understanding of the invention and to demonstrate its usefulness.

EXAMPLE I

In the runs which are shown in the Table I commercial kraft pulp at different stages in the kraft bleaching process for both hardwood type (aspen) pulp (H), and softwood (coniferous) pulp (S) were treated at 85° C. for two hours with brightening solutions consisting of an aqueous solution of tertiary butyl hydroperoxide and sodium hydroxide. In each run, an 18 gram sample of pulp (consisting of 4 grams of pulp, on an oven dried basis, and 14 grams of water) was treated with a brightening solution consisting of water containing 10 weight percent tertiary butyl hydroperoxide and 4 weight percent sodium hydroxide. In run 1 the amount of the brightening solution was 16 ml. so that the amount of tertiary butyl hydroperoxide employed was 1.6 grams or 40 weight percent of the weight of oven dried pulp and the amount of sodium hydroxide was 0.64 gram or 16 weight percent. In runs 2, 3, and 4 the amounts of brightening solution were 8, 4, and 2 ml. respectively. The amounts of tertiary butyl hydroperoxide based on the oven dried pulp were 20, 10, and 5 weight percent respectively. Handsheets of the brown stock, chlorinated pulp (C), chlorinated and extracted pulp (CE), chlorinated, extracted and hypochlorite pulp (CEH), and chlorinated, extracted, hypochlorite, and chlorine dioxide pulp (CEHD) as received were made in the conventional manner.

The Photovolt reflectances (compared to a standard magnesium oxide block as 100) were measured and compared with handsheets made from the pulps in runs 1, 2, 3, and 4. The results obtained are set forth in Table I.

In this and the other examples herein the handsheets were made in conventional manner by transferring the pulp to a Buchner funnel provided with a filter paper. The brightening solution was removed by suction and the pulp washed with several volumes of water to assure complete removal of the solution. The wet handsheet was oven dried at 100° C. under vacuum.

Unreacted tertiary butyl hydroperoxide and sodium hydroxide although known to be present at significant levels in the wash waters, were not recovered but, as shown in a later example, could be recycled.

TABLE I.—PHOTOVOLT REFLECTANCES

Pulp	Pulp as received	Run 1, 40% TBHP, ¹ 16% NaOH	Run 2, 20% TBHP, 8% NaOH	Run 3, 10% TBHP, 4% NaOH	Run 4, 5% TBHP, 2% NaOH
Brown stock (H)...	34	80	79	65	54
Brown stock (S)...	30	82	66	55	46
C (H).....	45	88	87	73	68
C (S).....	33	86	78	65	53
CE (H).....	51	90	88	83	76
CE (S).....	40	85	87	80	74
CEH (H).....	79	94	95	92	91
CEH (S).....	74	92	96	92	91
CEHD (H).....	91				
CEHD (S).....	91				

¹ TBHP is tertiary butyl hydroperoxide.

It was found that the pH of the brightening solution and the pulp at the start of the treatment was 10 or slightly higher and after treating the pH had dropped to about 9. It will be seen from these data that a 5 percent tertiary butyl hydroperoxide treat gives superior improvement in brightness compared with the corresponding prior art treat. For example, when hard wood brown stock is chlorinated the Photovolt reflectance is raised from 34 to 45, whereas in run 4 it will be seen that the reflectance is raised from 34 to 54. Similarly, it will be seen from run 4 that a CEH pulp can be brightened with a 5 percent tertiary butyl hydroperoxide treat to the same brightness obtained with conventional chlorine dioxide treating of the CEH pulp. Run 2 shows that a 20 percent tertiary butyl hydroperoxide treat gives superior results on a CEH pulp to anything that can be obtained commercially with chlorine dioxide.

Because of the particular interest in replacing chlorine dioxide in kraft bleaching three additional runs (5, 6, and 7) were carried out at levels of 2.5 percent, 1.0 percent, and 0.5 percent tertiary butyl hydroperoxide with 1.0 percent, 0.4 percent, and 0.2 percent respectively of sodium hydroxide in the same manner as has been described in obtaining the data in Table I. For the hardwood CEH pulps the reflectances obtained were respectively 87, 84, and 85 and the softwood reflectances were 85, 81, and 80 respectively. These experiments show that with as little as 0.5 percent tertiary butyl hydroperoxide and 0.2 percent sodium hydroxide brightening can be obtained.

EXAMPLE II

In order to show the effect of time and temperature a run for 6 hours at 50° C. using in the charge 5 weight percent tertiary butyl hydroperoxide and 2 weight percent sodium hydroxide based on the weight of oven dried pulp was carried out in the same manner as run 4. In Table II the Photovolt reflectance results on the handsheets of this run, designated run 8, are compared with those obtained at 85° C. for 2 hours in run 4.

TABLE II

Pulp	Run 8, 6 hrs., 50° C.	Run 4, 2 hrs., 85° C.
Brown stock (H)...	55	54
Brown stock (S)...	44	46
C (H).....	67	68
C (S).....	54	53
CE (H).....	75	76
CE (S).....	69	74
CEH (H).....	88	91
CEH (S).....	87	91

It will be seen that substantially the same results are obtained with the longer time at the lower temperature except in treating the CEH pulp where the D stage is being replaced. Here the shorter time and higher temperature is somewhat more preferable.

EXAMPLE III

A run was carried out in which the same pulps employed in Example I were treated in two successive stages for 6 hours at 50° C. in each stage charging 8.1 percent tertiary butyl hydroperoxide and 3.6 percent sodium hydroxide to each stage. The first treating solution was merely drained from the pulp between the stages. Thus,

the total treat amounted to 16.2 weight percent tertiary butyl hydroperoxide and 7.2 weight percent sodium hydroxide based on the oven dried weight of pulp. The Photovolt reflectances of the handsheets obtained in this run 9 are compared with the one stage treatment from Example I, run 2, wherein 20 percent tertiary butyl hydroperoxide and 8 percent sodium hydroxide were employed. The Photovolt reflectance results obtained are shown in Table III.

TABLE III

Pulp	Run 9, 2-stage, 16.2% TBHP, 7.2% NaOH	Run 2, 1-stage, 20% TBHP, 8% NaOH
Brown stock (H)....	77	79
Brown stock (S)....	77	66
C (H).....	84	87
C (S).....	82	78
CE (H).....	87	88
CE (S).....	82	87
CEH (H).....	92	95
CEH (S).....	93	96

It will be seen that the 2-stage treatment produces substantially the same results with approximately a 25% reduction in the total amount of brightening compounds employed. It should be noted that the single stage run at 85° C. for 2 hours as shown by Example II is at slightly more preferred conditions so that if the 2-stage process had been carried out at the higher temperature and shorter time equally good or superior results could be obtained.

EXAMPLE IV

Four runs were made on both the hardwood and softwood CE pulps at 100° C. for from 1 to 6 hours using 5 weight percent tertiary butyl hydroperoxide and 2 weight percent sodium hydroxide based on the oven dried pulp and compared with runs at 85° C. (run 4, Example I) and 50° C. (run 8, Example II). The Photovolt reflectances of the handsheets from these treatments are shown in Table IV.

TABLE IV

Pulp	Run 10, 100° C., 1 hr.	Run 11, 100° C., 2 hrs.	Run 12, 100° C., 3 hrs.	Run 13, 100° C., 6 hrs.	Run 4, 85° C., 2 hrs.	Run 8, 50° C., 6 hrs.
CE (H)....	73	76	75	75	76	75
CE (S)....	66	73	70	67	74	69

These data show that the higher temperatures above the preferred 85° C. do not give better results, but also show that time and temperature are not extremely critical factors thus adding to the flexibility of the process.

EXAMPLE V

A series of runs were carried out wherein the brightening solution recovered from a previous run was fortified with additional tertiary butyl hydroperoxide and sodium hydroxide for treatment of an additional quantity of pulp in order to show that a recycle operation could be suitably employed by the method of the instant invention.

In the first run, 4 grams of hardwood CEH pulp on an oven dried basis containing sufficient water to give 16.3 grams was treated with a brightening solution containing 10 weight percent tertiary butyl hydroperoxide and 4 weight percent sodium hydroxide in an amount such that

the tertiary butyl hydroperoxide amounted to 10 weight percent based on the oven dried weight of the pulp, i.e. 4 grams of solution was employed. Additional water was added to give a total charge weight of 30 grams. This mixture was heated at 85° C. for 2 hours and thereafter the pulp was filtered to remove the brightening solution. An aliquot portion of the filtrate was titrated to determine the residual amount of tertiary butyl hydroperoxide and sodium hydroxide in the solution. Additional brightening solution was then added to the filtrate together with water to give a second solution substantially the same as the solution for the first cycle for treating a second 4 gram pulp sample. This procedure was repeated 6 times. The Photovolt results on the handsheets made from each treated pulp sample is shown in Table V.

TABLE V

Cycle No.:	Photovolt reflectance
1	92
2	90
3	90
4	90
5	89
6	91

It was found that approximately 3.0 weight percent tertiary butyl hydroperoxide based on the oven dried pulp was consumed per cycle and 1.5 weight percent sodium hydroxide was consumed per cycle. A similar sample of this hardwood CEH pulp was treated with 1.5 weight percent chlorine dioxide to give a Photovolt reflectance of 91. Thus, it was established that the tertiary butyl hydroperoxide-sodium hydroxide brightening solution could be recycled with a 3 percent consumption of tertiary butyl hydroperoxide as compared with a 1.5 percent consumption of chlorine dioxide. At present commercial prices there is only a small saving in chemical cost using the method of the instant invention, although all of the aforementioned pollution, toxic, and hazardous disadvantages of using chlorine dioxide are avoided.

Subsequent experiments utilizing somewhat more refined brightening solution recovery techniques indicated that the tertiary butyl hydroperoxide consumption was actually less than the 3 percent value obtained in the original runs.

These recycled runs also demonstrated that the unconsumed brightening solution can be recovered and reused without build up of interfering compounds and without loss of brightening efficiency thus rendering the invention commercially attractive.

The results set forth in the foregoing examples demonstrate that the method of the instant invention is easily carried out without the use of expensive corrosion-proof bleaching vessels which in an ordinary commercial paper mill cost on the average about one million dollars per stage. The necessity for precision metering equipment is avoided as well as the use of toxic and hazardous chemicals.

In all of the runs of the foregoing examples there was no loss of pulp yield, whereas in the conventional CEHD process there is cellulose degradation by the Cl₂, NaOH, NaOCl and ClO₂, in addition to the production of polluting chlorinated products.

In the commercial plants the brightness increase for the stages are not the maximum obtainable but instead result from economic, yield and overtreatment (cellulose

degradation) consideration. For example ClO₂ bleaching above a 91 reflectance is possible but is not practiced commercially since it is too expensive and introduces the problem of forming chlorinated compounds both water-soluble (waste disposal problems and yield loss) and water-insoluble products which cause color reversion and strength loss in the paper.

The results shown herein in which the chlorine dioxide treating stage has been replaced demonstrate that much higher brightnesses, for example 96 Photovolt reflectances, are obtainable without incurring any of these problems. Thus the particular embodiment of this invention wherein the pulp is pre-bleached by conventional methods to the chlorine dioxide stage and thereafter brightened with the aqueous alkaline solution of tertiary butyl hydroperoxide constitutes one of the most important and beneficial embodiments of the invention.

We claim:

1. A method for the brightening of kraft pulp which comprises contacting the pulp with an aqueous solution consisting essentially of tertiary butyl hydroperoxide and sodium hydroxide or sodium carbonate to provide a pH of between 8 and 10.5, said contacting being at a temperature in the range of from 20° C. to 100° C.

2. The method according to claim 1 wherein the temperature ranges from 70° C. to 85° C.

3. The method according to claim 1 wherein the aqueous solution contains from 0.5 to 50 weight percent of tertiary butyl hydroperoxide based on the weight of the dry pulp.

4. The method according to claim 3 wherein the tertiary butyl hydroperoxide ranges between 5 weight percent and 40 weight percent.

5. The method according to claim 1 wherein the kraft pulp being treated is brown stock.

6. The method according to claim 1 wherein the kraft pulp has been chlorinated and extracted with sodium hydroxide.

7. The method according to claim 1 wherein the kraft pulp being contacted has been pre-bleached to the chlorine dioxide stage and is thereafter contacted with said tertiary butyl hydroperoxide solution.

8. The method according to claim 7 wherein the tertiary butyl hydroperoxide in the aqueous solution ranges between 5 and 20 percent by weight based on the weight of the dry pulp.

9. The method according to claim 1 wherein the pH ranges between 9 and 10.5 and is obtained by the use of sodium hydroxide in the aqueous solution.

References Cited

UNITED STATES PATENTS

1,767,543	6/1930	McKee et al.	8-111
3,467,575	9/1969	Wayman et al.	162-78
3,458,394	7/1969	Yiannos et al.	162-76

OTHER REFERENCES

Noller: Chemistry of Organic Compounds, 1951, pp. 792-793.

S. LEON BASHORE, Primary Examiner

A. L. CORBIN, Assistant Examiner

U.S. Cl. X.R.

8-111; 162-89