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BLEACHING OF LIGNOCELLULOSIC MATERIALS WITH OXYGEN IN THE PRESENCE OF A PEROXIDE

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No Drawing. Continuation-in-part of abandoned applications Ser. No. 34,543, May 4, 1970, and Ser. No. 145,567, May 20, 1971, the latter being also a continuation-in-part of the former. This application June 18, 1971, Ser. No. 154,689
Int. Cl. D21c 9/16
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ABSTRACT OF THE DISCLOSURE

The rate at which sulfate-process pulp is brightened by oxygenated aqueous medium is accelerated by the presence in the medium of a dissolved peroxide when the pH of the medium is in excess of 11.

This is a continuation-in-part of my copending application Ser. No. 34,543 filed on May 4, 1970, and its continuation-in-part application Ser. No. 145,567 filed on May 20, 1971, now both abandoned.

The present invention relates to the manufacture of paper pulp. More particularly, it relates to an improvement in the bleaching of sulfate process lignocellulose in oxygenated alkaline aqueous medium.

Lignocellulose is cellulose which carries a sufficient amount of ligning substituents to render it unacceptable for some papermaking purposes. Sulfate process lignocellulose is lignocellulose which has been produced by digestion of wood cellulose with sodium hydroxide and sodium sulfide, and differs in certain respects from the lignocellulose produced by other processes. Hoh, U.S. Pat. No. 3,382,149, discloses the treatment of sulfite pulp with alkaline hydrogen peroxide solution, with or without alkali pretreatment of the pulp. While the pulp becomes brighter as a result of the treatment, no lignin is removed therefrom. It is known that lignocellulose can be brightened by the action of an aqueous alkaline medium having a temperature of about 50° C.–150° C. and containing dissolved oxygen under pressure. The oxygen severs the bonds which connect the lignin substituents to the cellulose and the alkali carries the released lignin substituents (which are acidic) into solution. In the art, the process is termed "bleaching."

It is a disadvantage of the process that the oxygen causes partial depolymerization of the cellulose, decreasing the strength which paper made therefrom would otherwise possess.

The process is performed batchwise in large pressure vessels and is slow. The time required in any instance to effect a given amount of bleaching depends chiefly upon the temperature and pressure of the oxygen. High temperatures and high oxygen pressures favor rapid and extensive liberation of the lignin substituents, but depolymerize the cellulose to such an extent as to seriously decrease the value of the cellulose for papermaking purposes.

The discovery has now been made that the rate of which the aforesaid bleaching occurs is accelerated at any given temperature and oxygen pressure when the aqueous medium has a content of an alkali-soluble peroxide (i.e., a peroxide which is soluble in aqueous alkali solution), and when the pH of the medium is in excess of 11. The invention accordingly permits the duration of exposure of the cellulose to oxygen to be decreased with decrease in the depolymerization of the cellulose for attainment of any given improvement in brightness, and increases the daily output of any given plant.

Furthermore, it permits superior bleaching to be achieved under normal commercial conditions. Better bleaching is achieved by the use of oxygen and a peroxide in combination than is accomplished by either used separately or by both in sequence. It appears, therefore, that in the process the water-soluble peroxides act synergistically with the oxygen, functioning both as a bleaching reagent and as an accelerator of the bleaching action of the oxygen. The invention thus permits a maximum level of brightness to be attained more rapidly than would otherwise be the case.

It is a feature of the invention that the oxygen-peroxide combination is effective at very low oxygen pressure. Good results have been obtained merely by bubbling oxygen through an aqueous alkaline suspension of the pulp containing peroxide, the absolute pressure of oxygen in the process being only a few pounds per square inch. The process therefore can be performed without need of a pressure vessel.

The foregoing beneficial results are achieved only when the pulp under treatment is a sulfate process pulp, and preferably when the pulp is a kraft pulp (a sulfate process pulp under-cooked to produce a dark-colored pulp of exceptional strength). The use of peroxide as an additive in the alkali-oxygen bleaching of other pulps does not produce a significant benefit. As a practical matter, the process of the present invention is limited to the bleaching of kraft pulps.

The invention does not require the use of any specific amount of peroxide. In general, the beneficial effect of peroxide is proportional to the amount introduced into the aqueous medium and to the length of time the fibers are in contact therewith.

As a practical matter, we prefer to add an appropriate amount of peroxide to the water intended for use as the aqueous medium in the process. A suitable amount of peroxide can be found by laboratory trial, employing as a start an amount shown in the examples below. We have found that 0.2% peroxide, calculated as H_2O_2 and based on the dry weight of the fibers, produces a noticeable acceleration in the rate at which the lignin is liberated, so that evidently there is no amount however small, which will not impart some improvement. The maximum practical amount of peroxide appears to be about 15%, as larger amounts do not appear to impart correspondingly larger improvements. An amount within the range 0.5%–5% generally produces satisfactory results. Within this range, it is preferred that the amount of peroxide be sufficient so that at least some peroxide remains in the aqueous medium after the bleaching process has been completed.

The peroxide may all be added at the start (immediately prior to introducing the pulp into the pressure vessel), or it may be injected into the pressure vessel as the bleaching proceeds. It is within the scope of the invention to generate the peroxide in the pulp during the bleaching step. Thus, peracetic acid can be generated, for example, by adding hydrogen peroxide and acetyl chloride or acetic anhydride to the pulp, and sodium peroxide by adding hydrogen peroxide. Similarly, t-butylhydroperoxide can be generated from hydrogen peroxide and ti-butyl chloride. Because of the alkalinity of the pulp the peroxides are at least partly in ionized form.

No special steps need be taken to decompose or remove the residual peroxide on completion of the bleaching. The amount ordinarily left is so small, and its life so short, that it hardly affects the cellulose. It is customary to wash the pulp after the bleaching, and any residual per-

oxide is removed at that time. In the absence of a washing step, the peroxide is removed with the white water when the pulp is used for the manufacture of paper.

In the process, we have found that the action of the peroxide is very slight until the pH of the pulp is raised to about 11, at which point the peroxide commences to exert its synergistic action on the oxygen-pulp bleaching reaction. The effectiveness of the peroxide increases as the pH is increased beyond 11, and we therefore prefer to perform the bleaching at a pH as high as practical (about 13). Above pH 13 the bleaching action of the oxygen-peroxide combination proceeds rapidly, and alkali deterioration of the cellulose is not an important consideration.

In the process, the pressure of the O_2 oxygen may be high, up to the point where it causes danger of combustion (approximately 200 lb./in.^{2} absolute). A pressure in the range of 50–150 lb./in.^{2} is preferable as providing very rapid bleaching with little danger of combustion. If preferred, the O_2 oxygen pressure may be less than atmospheric, down to about 2 lb./in.^{2} absolute. In practice we have obtained good results simply by bubbling air at atmospheric pressure through the aqueous alkaline medium (oxygen pressure approximately 3 lb./in.^{2} absolute), so that that pressure is preferred. As a result the use of strong pressure vessels become unnecessary, and deploymerization of the cellulose occurs to at most a negligible extent.

The invention is further described in the examples which follow. These examples are best embodiments of the invention and are not to be construed as limitations thereon.

EXAMPLE 1

The following illustrates the process of the present invention performed on a laboratory scale.

(A) A laboratory rocking autoclave is charged with 6 g. (dry basis) of hardwood kraft pulp having a brightness as determined by reflectance under a General Electric glossmeter, of 26.6%, 293 ml. of water containing 0.264 g. of t-butylhydroperoxide (4.1% on the dry weight of the fibers), and 1.23 g. (7.5 millimols) of trisodium phosphate as alkali. The autoclave is sealed and heated to 95° C., and pure oxygen is supplied under a pressure of 120 lb./in.^{2} for 1.5 hours. The pulp is then removed and washed with hot water. It has a brightness of 61.4%.

(B) The procedure is repeated except that the peroxide is omitted. The pulp after washing has a brightness of 50.7%.

(C) Procedure A is repeated except that the oxygen is omitted. The brightness of the pulp after washing is 55.4%, showing that the oxygen and the peroxide cooperate to provide a result better than the results provided by the two materials acting separately.

(D) The procedure of run A is repeated with oxygen omitted and the resulting pulp is treated with oxygen in the manner of run A but with peroxide omitted. The brightness of the resulting pulp after washing is 48.2%, showing that it is critical for the pulp to be treated with oxygen and peroxide simultaneously.

EXAMPLE 2

The procedure of run A of Example 1 is repeated successively with equal weights of hydrogen peroxide, sodium peracetate, sodium m-chloroperbenzoate and cumene hydroperoxide being employed in place of the t-butylhydroperoxide. Results are substantially the same.

EXAMPLE 3

The following illustrates the process of the present invention using a peroxide which is generated in situ while the pulp is under oxygen pressure.

The procedure of run A of Example 1 is repeated except that 0.3 g. of tetrahydrofuran is added in place of the t-butylhydroperoxide. The oxygen converts part of the tetrahydrofuran to α-tetrahydrofuranhydroperoxide which acts as promoter of the bleaching effect of the oxygen in the same manner as the t-butylhydroperoxide.

EXAMPLE 4

The procedure of Example 3 is repeated except that the tetrahydrofuran is replaced by cumene. The oxygen converts part of the cumene to cumene hydroperoxide, and superior bleaching is achieved.

EXAMPLE 5

The following illustrates the effectiveness of the method of the present invention wherein the aqueous alkaline medium is oxygenated at atmospheric pressure.

A laboratory beaker is charged with 200 cc. of water at 90° C. containing 6 g. of hardwood kraft pulp having a brightness (reflectance) of 26.6%. To this is added concentrated NaOH solution containing 0.8 g. of NaOH and 0.3 g. of t-butylhydroperoxide. Oxygen is bubbled through the suspension by the use of a stainless steel sparger at the bottom of the vessel. The temperature is maintained at 90° C. and water is added from time to time to keep the level constant. After two hours the pulp is recovered by filtration, washed with water at room temperature and dried. The pulp has a brightness of 49.1%.

EXAMPLE 6

The procedure of Example 5 is repeated except that the t-butylhydroperoxide is replaced by 0.2 g. of hydrogen peroxide.

A similar brightening is obtained.

EXAMPLE 7

The following illustrates the practice of the present invention by the use of air under pressure in a closed vessel.

An aqueous fibrous suspension according to Example 3 (containing t-butylhydroperoxide and trisodium phosphate) is charged into a 600-cc. laboratory rocking autoclave. The autoclave is sealed and the contents are maintained at 90° C. for two hours under an air pressure of 40 lb./in.^{2}.

The autoclave is opened and the pulp is recovered, washed and dried. It has a brightness of 51%.

EXAMPLE 8

The following illustrates the effect of increasing amounts of peroxide.

To 100 cc. of water at 95° C. are added 18.25 g. of unbleached hardwood kraft pulp having a brightness (reflectance) of 29.6%, followed by 5.0% of NaOH and 1.0% of $MgCO_3$ based on the dry weight of the fibers. The suspension is charged into a laboratory rocking autoclave and kept under an oxygen pressure of 115 lb./in.^{2} (gauge) for 45 minutes. The autoclave is opened and the pulp is washed and dried and its brightness is determined. The procedure is repeated with t-butylhydroperoxide added in amounts shown in the table below.

The foregoing procedure is repeated except that pine kraft pulp having a brightness of 21.0% is used in place of the hardwood kraft pulp, and the autoclave treatment is extended to two hours.

Results are as follows:

Run No.	Pulp used	t-C_4H_9OOH added [1]	Brightness, percent	Kappa No.	Viscosity
1	Hardwood	None	51.5	8.1	11.3
2	do	1.0	52.1	8.6	
3	do	2.3	52.4	8.8	
4	do	3.3	61.0	7.5	
5	do	4.3	61.4	7.6	10.4
6	do	6.7	64.2	7.4	10.2
7	Pine	None	49.1	7.6	
8	do	6.2	53.5	7.9	

[1] Percent, based on dry weight of pulp.

EXAMPLE 9

The following illustrates the effect of pH on the action of peroxides as accelerators of the bleaching action of oxygen.

A laboratory beaker is charged with 200 cc. of water at 90° C. containing 6 g. of hardwood kraft pulp having a brightness (reflectance) of 26.6%. To this is added 0.3 g. of t-butylhydroperoxide, and the pH of the suspension is observed. Oxygen is bubbled through the suspension from a stainless steel sparger at the bottom of the beaker. The temperature of the suspension is maintained at 90° C., and water is added from time to time to keep the level constant. After two hours the pulp is recovered by filtration, washed with water at room temperature and dried. The reflectance (brightness) of the pulp is then determined by use of a glossmeter.

The procedure is repeated except that sufficient alkali is added in each instance along with the peroxide to adjust the pH of the suspension to the values shown in the table below. Results are as follows:

	Alkali added	pH	Brightness	
			Found	Percent improvement
Control			26.6	
Run No.:				
1	None	8.0	28.5	7.2
2	$NaHCO_3$	8.4	29.0	9.0
3	Na_2HPO_4	9.1	31.7	19.2
4	NH_3	10.9	33.1	24.3
5	Na_2CO_3	11.4	44.2	68.6
6	Na_3PO_4	11.6	48.7	83.3
7	KOH	13.0	49.0	84.0
8	NaOH	13.0	49.1	84.5

It will be observed that the percentage improvement rises much more rapidly above about pH 11 than below.

In the claims, "O_2" is used to designate oxygen such as is present in air, and to distinguish such oxygen from peroxide oxygen.

We claim:

1. In the manufacture of paper pulp by a process wherein sulfate process lignocellulose fibers are bleached in aqueous alkaline medium, a temperature of about 50° C.–150° C., and dissolved O_2 under a pressure of 2 to 200 lb./in.^{2} absolute: the improvement wherein said medium has a pH above 11 and contains a small but effective amount, less than 5% calculated as H_2O_2 based on the dry weight of the pulp, of an alkali-soluble peroxide as agent which accelerates the rate at which said fibers are bleached.

2. A process according to claim 1 wherein the fibers are kraft pulp fibers.

3. A process according to claim 1 wherein the medium is oxygenated with air at atmospheric pressure.

4. A process according to claim 1 wherein the medium is under an O_2 pressure of 50–150 lb./in.^{2} absolute.

5. A process according to claim 1 wherein the pH of said medium is above 13.

6. A process according to claim 1 wherein the peroxide is t-butylhydroperoxide.

7. A process according to claim 1 wherein the peroxide is hydrogen peroxide.

8. A process according to claim 1 wherein the peroxide is sodium peracetate.

9. A process according to claim 1 wherein the peroxide is sodium m-chloroperbenzoate.

10. A process according to claim 1 wherein the peroxide is cumene hydroperoxide.

11. A process according to claim 1 wherein the peroxide is α-tetrahydrofuranperoxide and said peroxide is generated in said pulp while said pulp is under O_2 pressure.

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