PURIFICATION OF FLUFFED OR SHREDDED PULP WITH CHLORINE DIOXIDE

Filed Oct. 23, 1968 3 Sheets-Sheet 1

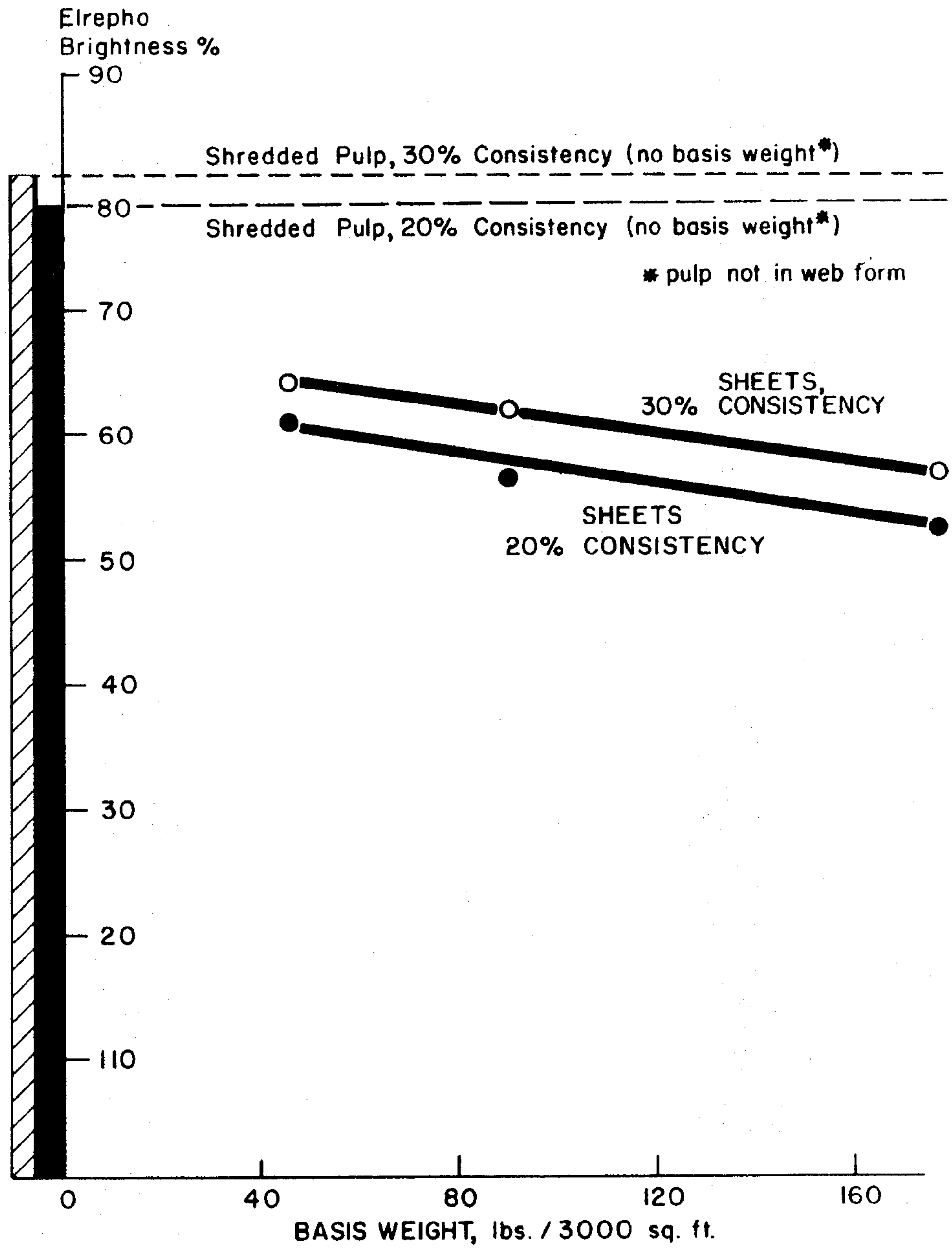

FIG. I

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PURIFICATION OF FLUFFED OR SHREDDED PULP WITH CHLORINE DIOXIDE

Filed Oct. 23, 1968 3 Sheets-Sheet 2

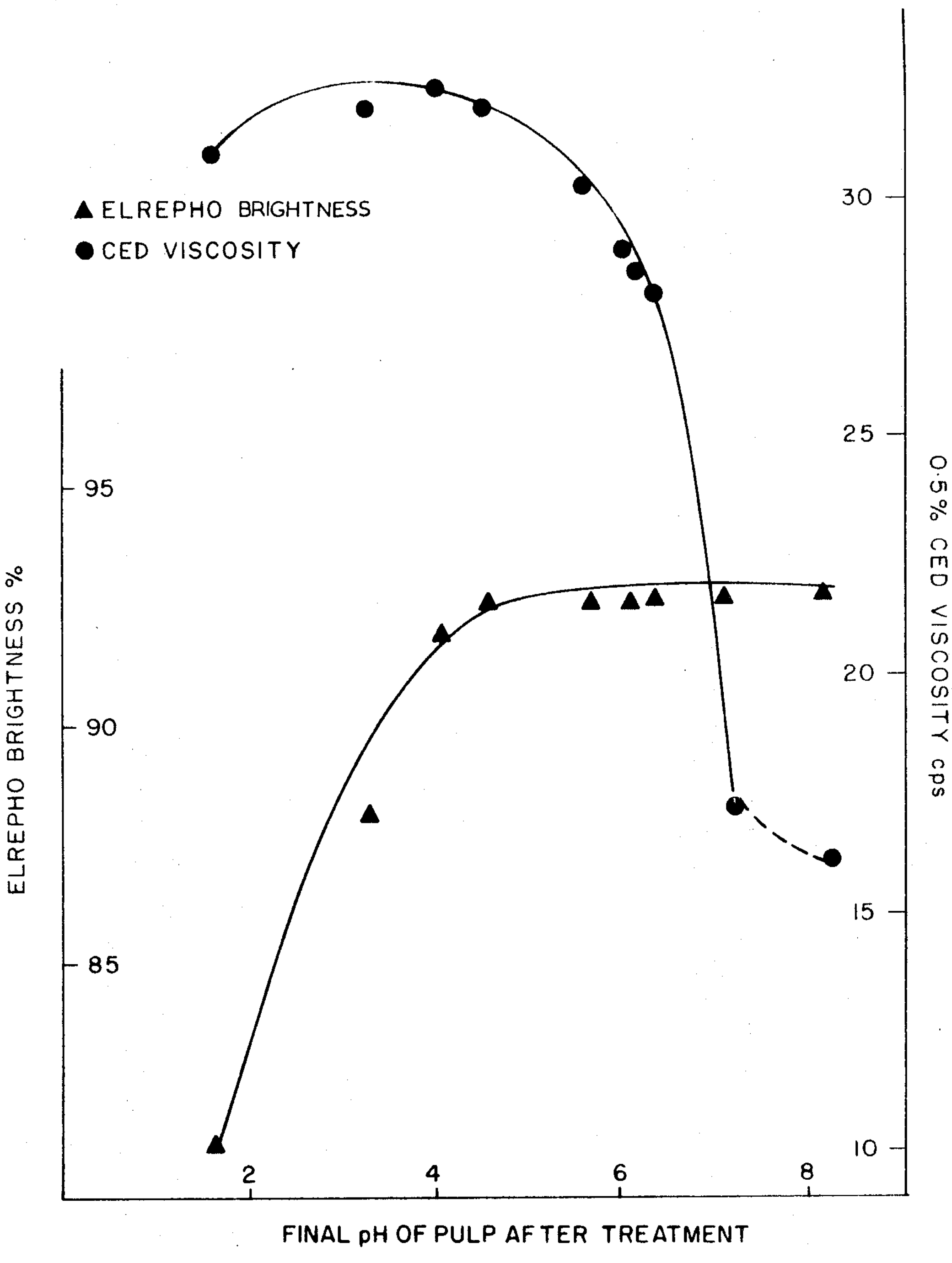

FIG. 2

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PURIFICATION OF FLUFFED OR SHREDDED PULP WITH CHLORINE DIOXIDE

Filed Oct. 23, 1968 3 Sheets-Sheet 3

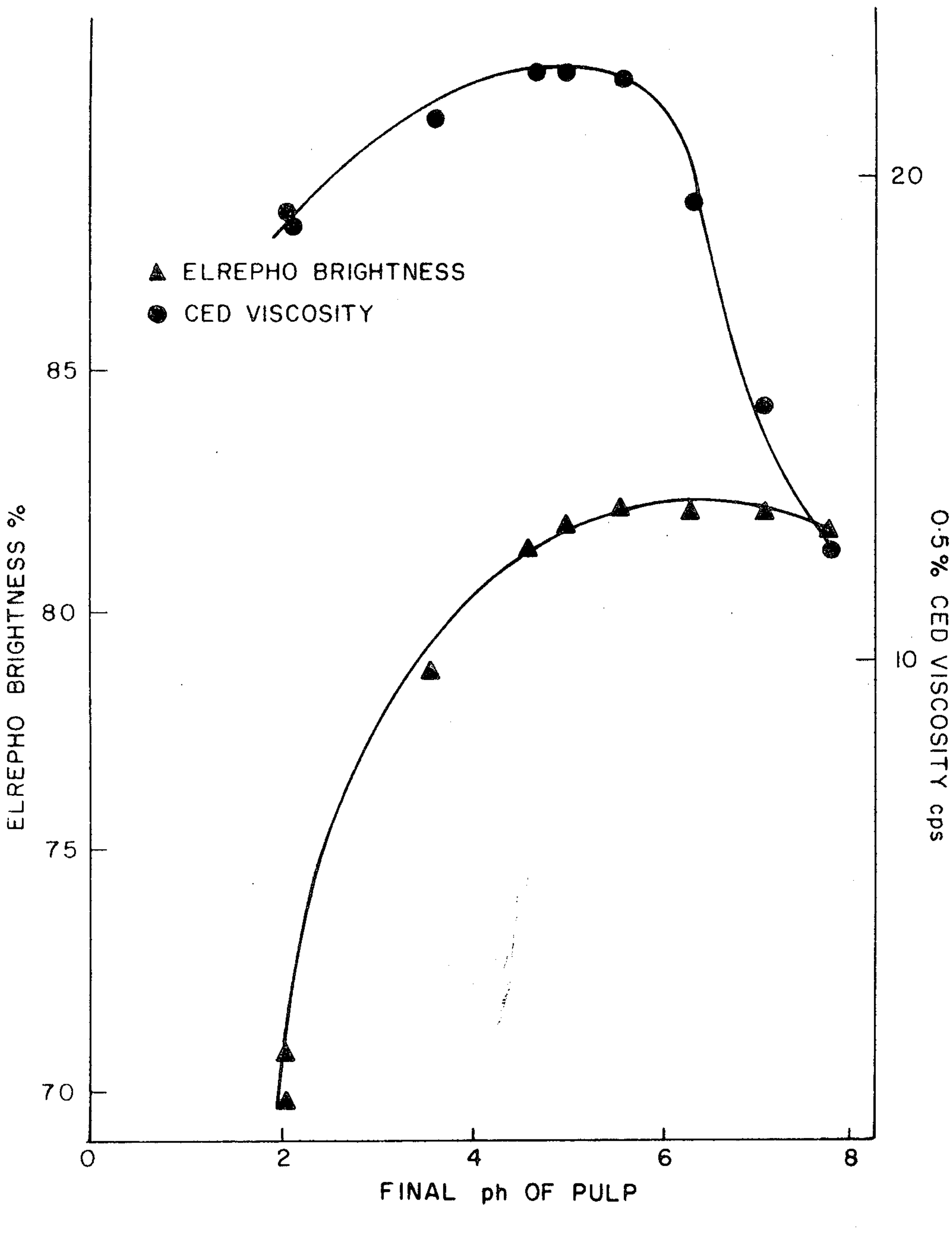

FIG. 3

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United States Patent Office

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PURIFICATION OF FLUFFED OR SHREDDED PULP WITH CHLORINE DIOXIDE

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Continuation-in-part of abandoned application Ser. No. 407,908, Oct. 30, 1964. This application Oct. 23, 1968, Ser. No. 769,879

Claims priority, application Canada, Aug. 7, 1964, 908,947

Int. Cl. D21c 9/14

U.S. Cl. 162—67 11 Claims

ABSTRACT OF THE DISCLOSURE

A process for bleaching chemical pulp which comprises adjusting the moisture content of the pulp to a level from 60 to 80%, preferably 60 to 70%, shredding or fluffing the pulp into fibres and fibre aggregates and then adding chlorine dioxide gas diluted with a non-reactive gaseous diluent such as nitrogen or steam to the shredded fluffed pulp mass. The partial pressure of the chlorine dioxide is desirably of 100 millimeters of mercury or less, the bleaching time is of the order of 5 to 30 minutes, and the temperature is desirably from 65 to 100° C. When the process is used to treat pulp in the third stage of a multistage bleaching process in which a partially delignified pulp obtained from an extraction stage following a chlorination delignification stage is treated with the chlorine dioxide the pH of the pulp is controlled suitably by the incorporation of a buffering agent into the pulp before contact with chlorine dioxide such that the final pH of the pulp, before washing is in the range of 2 to 6.5.

The present invention relates to a multistage process for bleaching a chemical cellulosic pulp and in particular to a relatively high speed treatment of the pulp during such a multistage bleaching process with gaseous chlorine dioxide.

This application is a continuation-in-part application of U.S. patent application No. 407,908 filed by the present applicants on Oct. 30, 1964, now abandoned.

In the multistage bleaching of a chemical pulp such as a kraft or sulphite pulp it is conventional to treat the pulp in one or more stages with an aqueous solution containing chlorine dioxide at a consistency from 6 to 15%, i.e. the pulp being in a form of a slurry containing 5.7 to 15.7 pounds of water per pound of dry pulp and at a temperature in the range of 65° to 85° C. to effect oxidation of said pulp. Treatment with chlorine dioxide must be continued for a period of from 3 to 5 hours in order to obtain satisfactory brightness of the pulp. Further, an aqueous solution of chlorine dioxide is used since it is substantially impossible in practice to achieve uniform treatment of a pulp slurry by means of gaseous chlorine dioxide. This oxidation treatment with chlorine dioxide is conventionally effected in the third stage of the multistage process on a partially delignified chemical pulp obtained from the extraction stage following a chlorinating delignification stage, and with a kraft pulp it may also be effected in the fifth stage of the multistage process following the fourth extraction stage. The aforesaid treatment of chemical cellulosic pulp with chlorine dioxide according to the aforesaid conventional process, involving the use of large volumes of water both in the pulp and in the aqueous solution of the chlorine dioxide, is a relatively slow and cumbersome process involving substantially high operating costs and large expenditures on capital equip-

ment required to handle the process over substantial periods of time.

In contrast thereto the present invention provides a process for the oxidative treatment of a chemical cellulosic pulp with chlorine dioxide which process is a relatively high speed process in which the pulp is contacted with chlorine dioxide over substantially reduced periods of time as compared with the conventional process and which involves the use of substantially reduced volumes of water for its operation.

According to the present invention therefore there is provided in the multistage bleaching of a chemical cellulosic pulp in which said pulp is subjected to an oxidative treatment with chlorine dioxide the improvement which comprises adjusting the moisture content of the pulp to a level of from 60 to 80%, shredding or fluffing the pulp into fibres and fibre aggregates, and exposing the shredded or fluffed pulp to chlorine dioxide gas diluted with a non-reactive gaseous diluent at a temperature of at least 65° C. for a period of time sufficient to obtain the desired brightness in said pulp.

Fluffed chemical cellulosic pulp (sometimes referred to as shredded chemical cellulosic pulp) is the product obtained by the fragmentation of a chemical cellulosic pulp into fibre and fibre aggregates or flocks, substantially each discrete fibre aggregate or flock being spongy, compressible and readily gas permeable. Each of said fibre aggregates or flocks is usually an average of ⅛ to 1" in diameter and presents a fluffed up dry appearance even with about 70 to 80% moisture in the cellulosic pulp. Thus reference herein to fluffing or shredding of the chemical cellulosic pulp is directed to a process of producing this pulp, the fragmentation being effected for example by the use of disc mills.

By adjusting the moisture content of the pulp to be in the range of 60 to 80% and preferably in the range 60 to 70% and by contacting the chlorine dioxide in gaseous form with the pulp, shredded or fluffed into fibre or fibre aggregates, it is possible by the process of the present invention to obtain a fast intimate contact of the chlorine dioxide with the interior of the fibres and fibre bundles and as a result to reduce the time necessary for obtaining the extent of reaction necessary for high brightness in the pulp. Thus it is possible according to the process of the present invention to reduce this time for obtaining high brightness in the pulp from a period of 3 to 5 hours as is required in the conventional process to the period from 5 to 30 minutes and thus provide a relatively high speed process for the chlorine dioxide oxidation of the pulp.

Due to the speed of the chlorine dioxide oxidative process of the present invention, the retention time in continuously operated reactors is greatly reduced which allows the use of much smaller equipment of lower capital cost. Also the presence of smaller quantities of pulp in process makes for more precise control of the operation. Furthermore, although reaction temperature is higher than in conventional processing, the sharp reduction in the quantity of water involved as a result of the use of a high pulp consistency results in substantial reduction of heat input to the reaction and in corresponding savings.

It has been further found that by the process of the present invention the amount of chlorine dioxide necessary to obtain a selected degree of brightness is reduced and in particular, it has been found possible to reduce the amount of chlorine dioxide by as much as 20% when compared with the aforesaid conventional process.

The oxidized pulp produced by the process of the present invention is found to be similar in all essential respects to the oxidized pulp produced by the aforesaid conventional process and in particular; has the advantage of better resistance to colour reversion than the oxidized pulp produced in the conventional process.

It is critical to the present invention that the pulp prior to contact with the gaseous chlorine dioxide be fluffed or shredded into the form of fibres or fibre aggregates to obtain the aforesaid intimate contact with the gaseous chlorine dioxide resulting in fast reaction time and thus high brightness over a short treatment period with the gaseous chlorine dioxide. Further, to effect this fluffing or shredding it is essential that the pulp have a consistency of at least 20% and preferably at least 30%; while the pulp may have a consistency of about 40% and still achieve the desirable results of the present invention, the obtention of a consistency of above 40% increases the cost of dewatering to an economically impractical extent.

It is necessary for use in the process of the present invention that the gaseous chlorine dioxide be diluted with a non-reactive gas as undiluted chlorine dioxide gas is subject to spontaneous explosion. Thus to reduce the risk of explosion, the gaseous chlorine dioxide is diluted with a non-reactive gas such as air, steam, nitrogen to a partial pressure not greater than 100 mm. of mercury and preferably about 30 mm. of mercury.

The temperature of the reaction is at least 65° C. to obtain a reasonably rapid reaction and the speed of reaction increases with increasing temperature; preferably the reaction temperature is in the range of 65° C. to 100° C. and more preferably 80° C. to 100° C. and even more preferably 90° C. to 100° C. For ease of control, it is expedient to operate at substantially 100° C., the temperature of saturated steam at atmospheric pressure.

The treatment of the chemical cellulosic pulp according to the present invention may be effected in the third stage of the multistage bleaching process for both kraft and sulphite pulps and may also be effected in the fifth stage for kraft pulps. In the third stage of the multistage bleaching process, where the plup is obtained from a caustic extraction stage following a chlorinating delignification stage, it has been found that, by using the process of the present invention, substantially higher brightness can be obtained under otherwise the same reaction conditions where the pH of the pulp is controlled in such a way that the final pH of the oxidized pulp is in the range 3.5 to 6.5 and preferably in the range 4 to 5.5. This control of the final pH of the oxidized chemical plup may suitably be effected by adding a buffering agent such as an alkaline metal salt of a weak acid, e.g. sodium carbonate, to the pulp before contact with the gaseous chlorine dioxide. It has been found however that when the inert gas diluted chlorine dioxide gas is contacted with pulp which contains an excessive amount of sodium carbonate e.g. 2.5 to 5% on o.d. pulp and the temperature is higher than about 85° C. the chlorine dioxide gas tends to violently decompose. Therefore, from a safety standpoint, to reduce the risk of this decomposition, high alkaline levels in the pulp should be in general avoided. Above and below the aforesaid pH range, it is found that the brightness of the pulp decreases rapidly under the same reaction conditions. In contrast thereto, with the fluffed pulp in the fifth stage of the multistage bleaching process, there is no necessity for controlling the pH of the pulp as the pH of the pulp has no appreciable effect upon the brightness of the pulp.

The present invention will be further illustrated by way of the following examples in conjunction with the accompanying drawings in which:

FIG. 1 is a graph of brightness against basis weight of handsheets of partly delignified sulphite pulp treated with chlorine dioxide according to the process of the present invention. It also compares the brightness levels obtainable on handsheets with those on shredded pulp at the same consistencies by the same process.

FIG. 2 is a graph of brightness and CED viscosity against final pH of a partially delignified sulphite pulp subjected to the process of the present invention, and

FIG. 3 is a graph of brightness and CED viscosity against final pH of a partially delignified Kraft pulp subjected to the process of the present invention.

EXAMPLE 1

An unbleached sulphite pulp from coniferous wood having a Roe chlorine number of 5.1 and a Kappa No. 24.4 was treated with gaseous chlorine at 30° C. The pulp was then washed, treated at 10% consistency with 2% by weight of sodium hydroxide for one hour at 60° C., and the pulp again washed. The semi-bleached pulp so obtained had a Kappa number of 0.8, a CED viscosity of 20.1 cps. and a brightness of 67.3 on the scale of the Elrepho meter. This pulp was divided into two equal portions and one portion of the pulp containing 60 g. dry fibre was dewatered to a 30% consistency by pressing, and then passing through a disc mill so as to shred and fluff the pulp into fibres and fibre aggregates and the fluffed and shredded pulp was placed in a glass tower 17" in length and 3½" in diameter. The tower was set in a bath maintained at 65° C. and gaseous chlorine dioxide diluted with nitrogen to a partial pressure of 30 mm. of mercury was passed into the tower until 0.6 gram of chlorine dioxide had been absorbed by the pulp, whence the pulp was held at 65° C. for 30 minutes. Unreacted chlorine dioxide was swept from the tower by a stream of air and absorbed in cold water. The quantity of chlorine dioxide recovered was by analysis found to be 0.216 gram and accordingly 0.384 gram of chlorine dioxide equal to 0.64% by weight of the pulp was found to have been consumed. The bleached pulp was found to have a brightness of 92.7 and a CED viscosity of 20.0 cps. The other portion of the pulp was treated with 1% by weight of chlorine dioxide at a consistency of 6% for two hours at 80° C. according to conventional techniques. It was found that chlorine dioxide equal to 0.12% by weight of the pulp remained unreacted such that 0.8% had been consumed and the brightness of the pulp so obtained was 91.3 and a CED viscosity was 20.8 cps.

It will be seen from the above example that by operating according to the process of the present invention, higher brightness was obtained in the pulp by a process which involved less consumption of chlorine dioxide in a substantially shorter period of time and at a lower temperature. The pulp obtained was of substantially the same CED viscosity which is indicative of the strength of the oxidized pulp.

EXAMPLE 2

An unbleached sulphite pulp was chlorinated, treated with sodium hydroxide and washed as described in Example 1. The semi-bleached pulp obtained had a Kappa number of 1.2, a CED viscosity of 28.0 cps., and a brightness of 66.2 on the scale of Elrepho meter. This semi-bleached pulp was dewatered to 30% consistency as in Example 1, fluffed and shredded by passage through a disc mill as in Example 1 and placed in a tower in a similar manner to Example 1. Steam at atmospheric pressure was passed upwardly through the tower and the flow of steam was continued until the temperature of the pulp as shown by a thermometer embedded in it was 89° C. when the flow of steam was diverted through an aqueous solution of chlorine dioxide contained in a gas washing bottle and containing chlorine dioxide equal to 1% by weight of the pulp. The chlorine dioxide was stripped from the aqueous solution by the steam and carried into the tower where it was absorbed on the pulp. The transfer of chlorine dioxide from the solution to the pulp was complete in five minutes and the steaming was discontinued. After a further five minutes unreacted chlorine dioxide was swept out of the tower with air and absorbed in water and from an analysis of the recovered solution the chlorine dioxide consumption by the pulp was calculated to be 0.62% by weight of the pulp and the pulp so obtained had a brightness of 83.2 and a CED viscosity of 29.2 cps. It will be seen from this example that after an extremely short oxidative treatment of the semi-bleached pulp with steam and chlorine dioxide the brightness of the pulp was increased by 17 points.

EXAMPLE 3

An unbleached sulphite pulp was partially delignified in a similar manner as in Example 1 by the following sequence of treatment; chlorination, water washing, extraction with sodium hydroxide and washing with water to neutrality.

The partially delignified pulp was divided into four different portions. The first portion of the pulp was treated with an aqueous solution of sodium carbonate (1% sodium carbonate on pulp) and shredded and fluffed as in Example 1 at 20% consistency and treated with gaseous chlorine dioxide. The second portion was pretreated with an aqueous solution of sodium carbonate in a similar manner as the first portion and shredded and fluffed at 30% consistency and treated with gaseous chlorine dioxide in a similar manner to the first portion. The third portion and the fourth portion were made into sheets in accordance with standard hand sheet making procedure, one set of sheets having an initial consistency of 25%, the other set having an initial consistency of 35%. The sheets were sprayed with an aqueous solution of sodium carbonate (1% sodium carbonate on pulp) to reduce the consistencies to 20% and 30% respectively, and the basic weight of the hand sheets was 44, 88 and 176 pounds per square foot. The sheets were then cut into 1" wide strips and treated with chlorine dioxide. All the pulp samples, fluffed and in sheet form, were treated with gaseous chlorine dioxide in an amount of 1% on pulp the chlorine dioxide being diluted with nitrogen to a partial pressure of 30 torr for a bleaching time of 30 minutes at 65° C. The results obtained are shown in FIG. 1 of the accompanying drawings in which it will be seen that with the shredded pulp which was not formed into hand sheets and therefore had a no basis weight, the brightness obtained was of the order of 20 points higher than that obtained with the hand sheets. In practice, as aforesaid, it is impossible to pass gaseous chlorine dioxide through a slurry of the pulp at normal consistency of up to 15% in a sufficient amount to obtain adequate oxidation of the pulp and therefore, for the purposes of comparison in this example, the pulp was dewatered to a higher consistency similar to the pulp treated according to the present invention and formed into hand sheets which made it available for treating with chlorine gas for oxidative brightening. Thus this example illustrates markedly the criticality of the shredding and fluffing of the pulp for obtaining improved brightness over a short period of time.

EXAMPLE 4

Unbleached news grade sulphite pulp having a Roe chlorine number of 9.6 was partially bleached by chlorination and extraction with sodium hydroxide as described in Example 1. The semi-bleached pulp so obtained had a Kappa number of 5.0 and a brightness of 54.7 on the scale of the Elrepho meter. One portion of the pulp was dewatered to 35% consistency by pressing and the pressed cake was sprayed with a solution containing sodium acetate equal to 2.46% by weight of the pulp and water sufficient to reduce the consistency to 30%. The pressed cake was then shredded and fluffed as in Example 1 and placed in a glass tower set in a water bath at 65° C. in a similar manner to Example 1. Chlorine dioxide diluted with nitrogen to a partial pressure of 30 mm. of mercury was passed into the tower until the moist pulp had taken up chlorine dioxide equal to 1% by weight of the dry weight of the pulp when the tower and its contents were maintained at 65° C. for a period of 5 minutes. Excess chlorine dioxide was then swept out of the tower by aeration and the amount swept out determined analytically whereby the chlorine dioxide consumed was calculated to be 0.51% by weight of the pulp. The final pH of the pulp was 4.95

and its brightness after washing and drying was 81.4. A second portion of the pulp was treated exactly as the first portion except no sodium acetate was added as a buffer to the pulp. The chlorine dioxide consumption was found to be 0.6% by weight on the pulp, the brightness was 76.9 and the final pH after the chlorine dioxide treatment was 2.5.

It would be seen that this example amply illustrates the criticality of the pH in the third stage of the multistage bleaching process as the increase in brightness by controlling the pH is of the order of 5 points.

EXAMPLE 5

Unbleached kraft pulp from coniferous wood was chlorinated and extracted with sodium hydroxide solution as in Example 1. The extracted pulp had a brightness of 31.2 and Kappa number 7.3. Portions of the extracted pulp were fluffed as in Example 1 at 20, 30 and 40% consistency and contacted with 1% by weight on the dry pulp of chlorine dioxide for a period of 30 minutes, the chlorine dioxide having a partial pressure of 30 mm. of mercury in nitrogen. The oxidations were run at three temperatures of 65° C., 80° C., and 92° C. respectively, and in some of the oxidations, sodium carbonate was added to the pulp in an amount to give a pH of about 4.5 after chlorine dioxide treatment. In other oxidations no buffer was employed and the final pH was 2.2. The brightness of the treated pulps are set out in the following Table I.

TABLE I.—BRIGHTNESS

	Unbuffered chlorine dioxide			Chlorine dioxide and sodium carbonate		
Consistency, percent	20	30	40	20	30	40
Temperature, ° C.:						
65	68.6	67.9	65.3	75.0	74.1	76.7
80	68.6	71.9	72.6	78.0	80.0	79.8
92	60.9	69.6	70.9	77.3	81.0	81.1
	Average end pH 2.2: average brightness 68.5			Average end pH 4.5: average brightness 78.1		

It will be seen from the above Table I that the advantages of the process of the present invention can be achieved at pulp consistencies of 20 to 40% and at temperatures upwardly of 65° C. and that the brightness obtained using a buffer is greater than the brightness obtained without the buffer in the third stage of the multistage bleaching process by about 10 points.

EXAMPLE 6

An unbleached sulphite pulp from coniferous wood having a Roe chlorine number 7.9, Kappa number 33.0 and CED viscosity 35.6 cps. was chlorinated, washed, extracted with dilute sodium hydroxide and washed again in a similar manner to Example 1. The partially delignified pulp had Kappa number 1.0, CED viscosity 33.1 cps. and an Elrepho brightness of 57.7%.

(A) A portion of the chlorinated, extracted and washed pulp was pressed to 35% consistency. The pressed pulp was sprayed with a solution containing sodium carbonate (1 percent Na_2CO_3 on o.d. pulp) and water sufficient to reduce the pulp consistency to 30%, i.e. moisture content of 70%. The pulp was then shredded into fibre and fibre aggregates, and placed in a tower which was set in a bath and the temperature maintained at 80° C. Chlorine dioxide diluted with nitrogen to a partial pressure of 30 torr was passed into the tower until 0.6% ClO_2 on pulp o.d. basis was passed into the tower and the pulp was held at 80° C. for 30 minutes. Unreacted chlorine dioxide was removed from the tower by aeration and determined analytically. The chlorine dioxide consumed amounted to 0.58% ClO_2 on pulp o.d. basis. The final pH of the moist, bleached pulp was 5.2. A portion of the bleached pulp was washed, air dried, and the brightness measured. The brightness tabs were then placed in a hot air circulating oven at 105° C. for 1 hour, then conditioned in a constant atmosphere; relative humidity 50% at 70° F. The brightness after accelerated aging was measured and the brightness loss calculated. The brightness and the loss in brightness after aging are set out in the Table II below.

(B) A second portion of the same semi-bleached pulp was treated with one percent of its weight of chlorine dioxide at 10% consistency for 3 hours at 70° C. Chlorine dioxide, equal to 0.09% of the weight of pulp remained unreacted so that 0.91% ClO_2 had been consumed. As above the pulp was washed, dried, the brightness and loss in brightness were measured and the results are set out in the Table II below.

TABLE II

ClO_2 treatment	Brightness, percent Elrepho — After bleaching	Brightness, percent Elrepho — After aging	Brightness reversion percentage points
Shredded partially delignified pulp at 30% consistency treated with diluted gaseous ClO_2	92.8	88.2	4.6
Conventional aqueous ClO_2 treatment	92.2	85.9	6.3

It will be seen from Table II that the resistance of the fully bleached sulphite pulp produced by the process of the present invention to brightness reversion is greater than that produced by the conventional oxidation process with chlorine dioxide.

EXAMPLE 7

An unbleached kraft pulp from coniferous wood having a Roe chlorine number 4.3, Kappa number 26.8, and 0.5% CED viscosity after acid chloride treatment 25.0 cps. was chlorinated, washed, extracted with dilute sodium hydroxide and washed again as in Example 1. The partially delignified pulp had a Kappa number 7.3, Elrepho brightness 31.2%, and 0.5% CED viscosity of 25.1 cps.

(A) A portion of the chlorinated, extracted and washed pulp was pressed to 35% consistency. The pressed pulp was sprayed with a solution containing sodium carbonate (1 percent Na_2CO_3 on o.d. pulp) and water sufficient to reduce the pulp consistency to 30%. The pulp was then shredded into fibre and fibre aggregates and placed in a tower which was set in a bath and the temperature was maintained at 92° C. Chlorine dioxide diluted with nitrogen to a partial pressure of 30 torr was passed into the tower until 1.0% ClO_2 on pulp o.d. basis was passed into the tower. The pulp was held at 92° C. for 30 minutes. Unreacted chlorine dioxide was removed from the tower by aeration and determined analytically and the chlorine dioxide consumed amounted to 0.85% ClO_2 on pulp o.d. basis. The final pH of the moist, bleached pulp was 5.4. A portion of the bleached pulp was washed, air dried, and the brightness measured. The brightness tabs were then placed in a hot air circulating oven at 105° C. for 1 hour, then conditioned in a constant-atmosphere, relative humidity 50% at 70° F. The brightness after accelerated aging was measured and the brightness loss calculated. The brightness and the loss in brightness after aging are set out in Table III.

(B) A second portion of the same semi-bleached kraft pulp was treated with 1.2 percent of its weight of chlorine dioxide at 10% consistency for 3 hours at 70° C. Chlorine dioxide, equal to 0.03% of the weight of pulp remained unreacted so that 1.17 percent ClO_2 had been consumed. As above, a portion of the pulp was washed, dried, the brightness and the loss in brightness were measured and the results are set out in Table III.

TABLE III

ClO_2 treatment	Brightness, percent Elrepho — After bleaching	Brightness, percent Elrepho — After aging	Brightness reversion percentage points
Shredded partially delignified pulp at 30% consistency treated with diluted gaseous ClO_2	82.3	77.8	4.5
Conventional aqueous ClO_2 treatment	82.1	77.0	5.1

It will be seen from Table III that a semi-bleached kraft pulp produced according to the process of the present invention also has a greater resistance to brightness reversion than for conventional pulp.

(C) A portion of the kraft pulp which had been bleached to 82.3 brightness with gaseous chlorine dioxide was extracted with sodium hydroxide using 0.3% NaOH on pulp at 60° C. and 10% consistency for 1 hour. The pulp was then washed, pressed to 30% consistency and shredded into fibre and fibre aggregates. The pulp was then placed in a tower, the tower and pulp was set in a bath and the temperature maintained at 92° C. Chlorine dioxide diluted with nitrogen to a partial pressure of 30 torr was passed into the tower until 0.25 percent ClO_2 on pulp o.d. basis was passed into the tower. The pulp was held at 92° C. for 30 minutes. Unreacted chlorine dioxide was removed from the tower by aeration and determined analytically. The chlorine dioxide consumed amounted to 0.16% ClO_2 on pulp o.d. basis. The pH of the moist, bleached pulp was 5.1. The bleached pulp was washed, air dried, and the brightness measured. The brightness tabs were then placed in a hot air circulating oven at 105° C. for 1 hour, then conditioned in a constant-atmosphere, relative humidity 50% at 70° F. The brightness after accelerated aging was measured and the brightness loss calculated. The brightness and the loss in brightness after aging are set out in Table IV.

(D) Samples of the kraft pulp which had been bleached to a brightness of 82.1 by conventional chlorine dioxide treatment were extracted with sodium hydroxide using 0.3% NaOH on pulp at 60° C. and 10% consistency for one hour. After washing, the pulp was treated with 0.35% of its weight of chlorine dioxide at 10% consistency for three hours at 70° C. Only a trace residual of chlorine dioxide remained after the bleaching period (0.34% chlorine dioxide or o.d. pulp was consumed). As above, the pulp was washed, air dried, and brightness and loss in brightness were measured and the results are set out in Table IV.

TABLE IV

ClO_2 treatment	Brightness, percent Elrepho — After bleaching	Brightness, percent Elrepho — After aging	Brightness reversion percentage points
Shredded partially delignified pulp at 30% consistency treated with diluted gaseons ClO_2	92.1	2.7	89.4
Conventional aqueons ClO_2 treatment	91.7	3.1	88.6

It will be seen from Table IV that a fully bleached kraft pulp produced by the process of the present invention has a greater resistance to brightness reversion than a conventional pulp.

EXAMPLE 8

Portions of the partially delignified sulphite pulp characterized by Kappa number 1.0, CED viscosity 33.1, Elrepho brightness 57.7%, were pressed to 35% consistency. In one test no Na_2CO_3 was employed and only water sufficient to reduce the pulp consistency to 30% was added to the pulp. The pulp was then shredded into fibre and fibre aggregates. In other tests increasing quantities of the sodium carbonate with sufficient water to reduce the pulp consistency to 30% was added to the pulp and then the pulp was shredded into fibre and fibre aggregates. Each sample of shredded pulp was placed in a tower, the tower was set in a bath and temperature maintained at 80° C. Chlorine dioxide diluted with nitrogen to a partial pressure of 30 torr was passed into the tower until 0.6% ClO_2 on pulp o.d. basis was passed into the tower. The pulp was held at 80° C. for 30 minutes. Unreacted chlorine dioxide was removed from the tower by aeration and the pH of the moist bleached pulp was measured for each of these samples. The bleached pulp was washed, air dried, the brightness and the CED viscosity determined on the dried pulp samples. The results obtained are given in Table V and in FIG. 2 of the accompanying drawings, which is a graph of the variation of brightness and viscosity with the final pH of the partially delignified pulp. It will be seen from FIG. 2 that the Elrepho brightness increases substantially as the final pH is increased from 1.65 to pH of 4. Maximum brightness was obtained with the gas phase chlorine dioxide bleaching on high consistency shredded pulp between the final pH range of 3.5 and 6.5 with a given amount of chlorine dioxide (0.6% on o.d. pulp) at a given temperature (80° C.) and at a given time (30 min.). It will also be seen from FIG. 2 that chlorine dioxide has only a small effect on viscosity between the final pH's of 1.65 and 6. At final pH values above 6 the viscosity begins to decrease quite rapidly as the final pH is increased. The viscosity of solutions of pulp in suitable solvents such as cupriethylenediamine is a function of the degree of polymerization of the cellulose, and although the mechanical properties of the fibre are not directly correlated with the viscosity, it can be seen from the values of the mechanical properties of the pulp, presented in Table IV, that the tensile and bursting strength of the pulp are reduced, accompanying the drop in viscosity as the final pH is increased above 7.

TABLE V.—BLEACHED SULPHITE PULP

High density gaseous ClO_2 stage			Strength properties at 300 CSF	
Final pH	Elrepho brightness, percent	CED viscosity, cps.	Breaking length (m.)	Burst factor
4.5	92.5	31.9	10,100	72
6.1	92.7	28.0	10,400	72
7.2	92.8	17.3	9,700	68
8.1	91.7	16.1	9,200	61

EXAMPLE 9

Portions of the partially delignified kraft pulp having Kappa number 7.3, 0.5% CED viscosity 25.1 cps., and Elrepho brightness 31.2%, were pressed to 35% consistency. In one test no carbonate was employed and only water sufficient to reduce the pulp consistency to 30% was added to the pulp. The pulp was then shredded into fibre and fibre aggregates. In other tests increasing quantities of the sodium carbonate with sufficient water to reduce the pulp consistency to 30% was added to the pulp and then the pulp was shredded into fibre and fibre aggregates. Each sample of shredded pulp was placed in a tower, the tower was set in a bath and temperature maintained at 92° C. Chlorine dioxide diluted with nitrogen to a partial pressure of 30 torr was passed into the tower until 1.0% ClO_2 on pulp o.d. basis was passed into the tower. The pulp was held at 92° C. for 30 minutes. Unreacted chlorine dioxide was removed from the tower by aeration and the pH of the moist bleached pulp was measured for each of these samples. The bleached pulp was washed, air dried, the brightness and the CED viscosity determined on the dried pulp samples. The results obtained are given in Table VI and in FIG. 3 of the accompanying drawings, which is a graph of the variation of brightness and viscosity with the final pH of the partially delignified pulp. It will be seen from FIG. 3 that the Elrepho brightness increases substantially as the final pH is increased from 1.9 to 4. Maximum brightness was

obtained with the gas phase chlorine dioxide bleaching on high consistency shredded pulp between the final pH ranges of 4 and 6.5 with a given amount of chlorine dioxide (1.0% on o.d. pulp) at a given temperature (92° C.) and at a given time (30 min.). It will also be seen from FIG. 3 that chlorine dioxide has only a small effect on viscosity between the final pH's of 2 and 6. At final pH values above 6 the viscosity begins to decrease quite rapidly as the final pH is increased. The viscosity of solutions of pulp in suitable solvents such as cupriethylenediamine is a function of the degree of polymerization of the cellulose, and although the mechanical properties of the fibre are not directly correlated with the viscosity, it can be seen from the values of the mechanical properties of the pulp, presented in Table VI, that the tensile and bursting strength of the pulp are reduced, accompanying the drop in viscosity as the final pH is increased above 7.

TABLE VI.—SEMI-BLEACHED KRAFT

High density gaseous ClO_2 stage			Strength properties at 300 CSF	
End pH	Elrepho brightness, percent	CED viscosity, cps.	Breaking length (m.)	Burst factor
3.5	79.8	20.3	12,200	93
5.0	82.3	22.0	12,300	101
6.3	82.1	19.5	12,400	98
7.2	82.0	15.3	11,600	92
7.8	81.7	12.3	11,150	90

We claim:

1. In a stage of a multistage bleaching process of a chemical cellulosic pulp in which stage the cellulosic pulp is treated in a single step with chlorine dioxide the improvement which comprises adjusting the moisture content of the pulp to a level from 60 to 80%, shredding or fluffing the pulp into fibers and fiber aggregates and exposing the shredded or fluffed pulp to chlorine dioxide gas diluted with a non-reactive gaseous diluent at a temperature of at least 65° C. for a period of time sufficient to obtain the required brightness in said pulp, the consistency of the pulp during said exposure being maintained substantially constant in the range 20 to 40%, and the pH of the pulp being controlled so that the final pH of the thus-treated pulp, before washing, is in the range 2 to 6.5.

2. A process as claimed in claim **1** in which the pulp has a moisture content from 60 to 70%.

3. A process as claimed in claim **1** in which the chlorine dioxide has a partial pressure not greater than a 100 mm. of mercury.

4. A process as claimed in claim **1** in which the chlorine dioxide has a partial pressure about 30 mm. of mercury.

5. A process as claimed in claim **1** in which the reaction is effected for a period of from 5 to 30 minutes.

6. A process as claimed in claim **1** in which the diluent is steam.

7. A process as claimed in claim **1** in which the temperature is from 65 to 100° C.

8. A process as claimed in claim **1** in which the temperature is from 90 to 100° C.

9. A process as claimed in claim **1** in which the pulp treated with the chlorine dioxide is obtained from a caustic extraction stage following a chlorinating delignification stage and the pH of the pulp is controlled such that the final pH thereof is in the range 3.5 to 6.5.

10. A process as claimed in claim **9** in which the pH is in the range 4 to 5.5.

11. A process as claimed in claim **9** in which the pH is controlled by the addition of an alkaline agent to the pulp before contact with the chlorine dioxide.

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