United States Patent

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[72] Inventors **Norman Liebergott**
Chomedy, Quebec;
Frederic H. Yorston, Montreal, Quebec;
Raimbault M. A. T. De Montigny, Baie D'Urfe, Quebec; John E. Tasman, Pointe Claire, Quebec, all of Canada

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[73] Assignee **Pulp and Paper Research Institute of Canada**
Pointe Claire, Quebec, Canada

[54] BLEACHING OF A LOW-DENSITY, SUBSTANTIALLY UNCOMPACTED, POROUS FLUFFED CELLULOSIC PULP

10 Claims, 9 Drawing Figs.

[52] **U.S. Cl.** **162/24,** 162/63, 162/65, 162/66, 162/67, 162/88
[51] **Int. Cl.** **D21b 1/16**
[50] **Field of Search** 162/24, 63, 65, 66, 67, 78, 87, 88, 100

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Primary Examiner—S. Leon Bashore
Assistant Examiner—Arthur L. Corbin
Attorney—Stevens, Davis, Miller & Mosher

ABSTRACT: The bleaching of chemical wood pulp at high consistencies with gaseous bleaching agents is performed by repeatedly contacting the pulp, at a consistency above 15 percent and while unsupported, with radial spaced breaker arms extending from a rotating shaft thereby producing a comminuted pulp of low density and a substantially uncompacted porous fluffed structure and thereafter bleaching the comminuted fluffed pulp at a consistency above 15 percent with a gaseous bleaching agent such as chlorine dioxide gas.

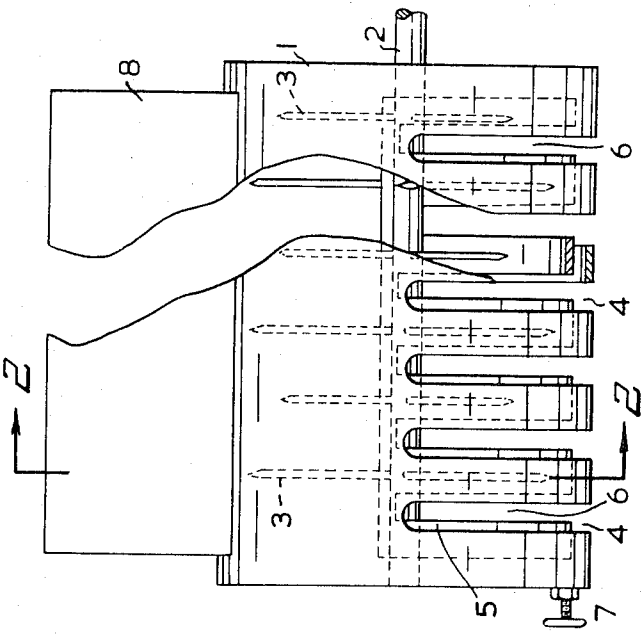


FIG. 1.

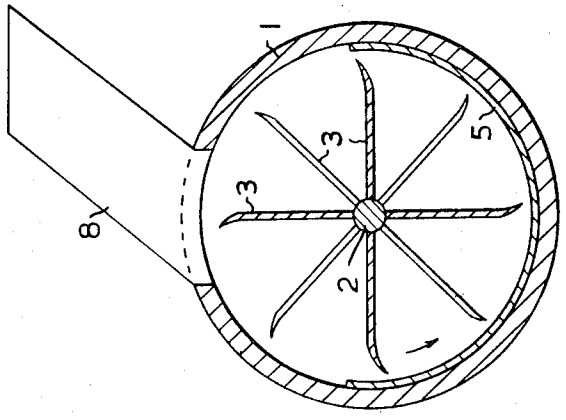


FIG. 2.

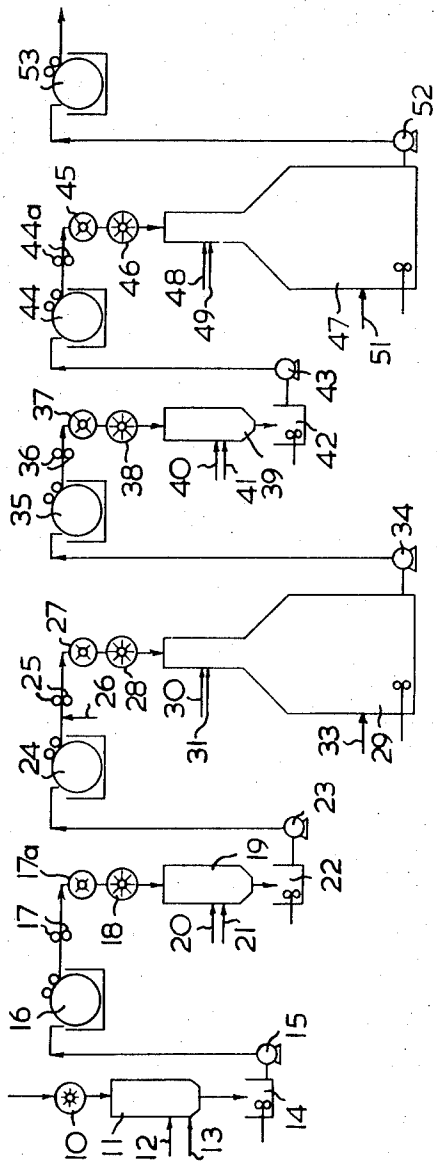

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Fig. 3.

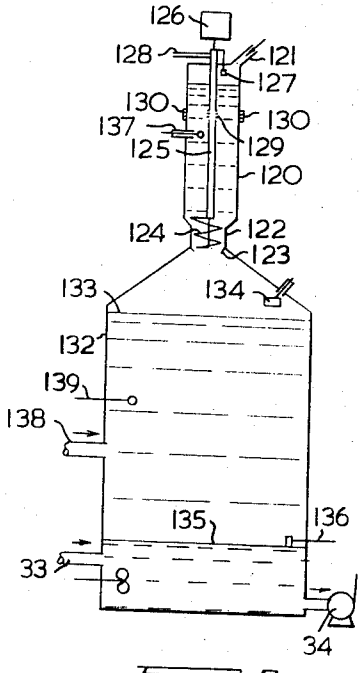

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FIG. 5.

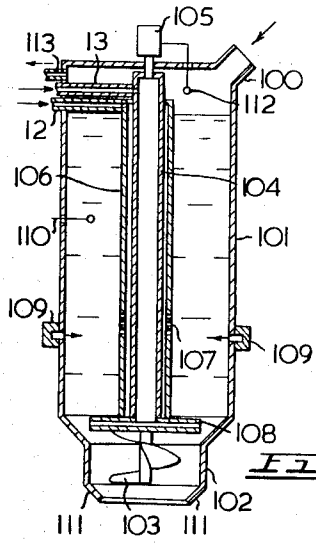

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FIG. 4.

FIG. 6A

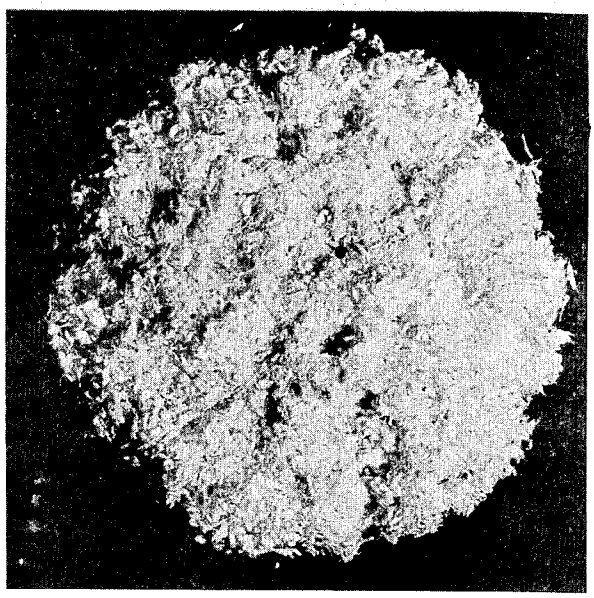
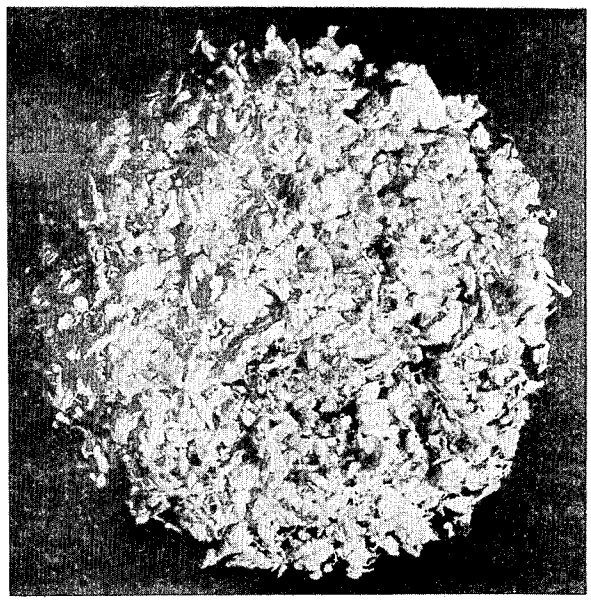


FIG. 6B



INVENTORS
NORMAN LIEBERGOTT
FREDERIC H. YORSTON
RAIMBAULT M. A. T. deMONTIGNY
JOHN E. TASMAN
Stevens, Davis, Miller & Mosher
ATTORNEYS

FIG. 7A

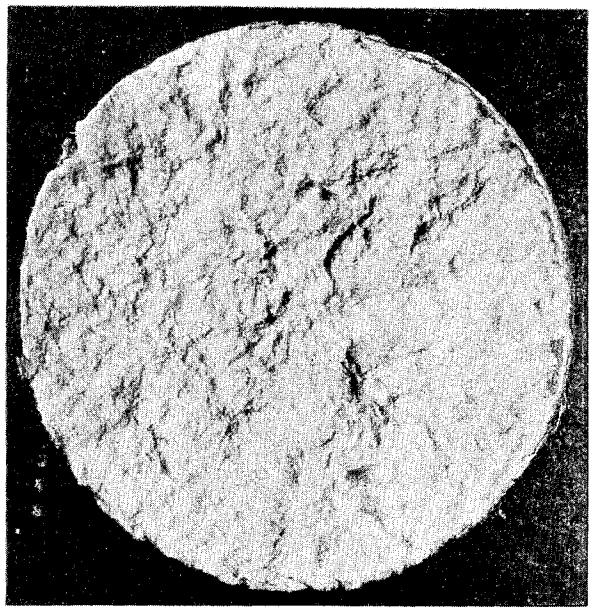


FIG. 7B



INVENTORS
NORMAN LIEBERGOTT
FREDERIC H. YORSTON
RAIMBAULT M. A. T. deMONTIGNY
JOHN E. TASMAN
Stevens, Davis, Miller & Mosher
ATTORNEYS

BLEACHING OF A LOW-DENSITY, SUBSTANTIALLY UNCOMPACTED, POROUS FLUFFED CELLULOSIC PULP

The present invention relates to the treatment of cellulosic fibrous pulp, particularly wood pulp, with a gaseous reagent and in particular relates to the comminution of the fibrous cellulosic pulp for use particularly in a multistage bleaching process in which it is contacted with a gaseous reagent.

In conventional practice unbleached wood pulp is bleached by treating it with a succession of reagents in aqueous solution, the order of addition of the reagents being most frequently chlorine, sodium hydroxide, and chlorine dioxide.

Thus, in the aforesaid multistage process the first operation for the removal of lignin and other encrustants, usually following the digestion stage and a subsequent washing stage in the kraft, soda or sulphite process consists in treatment of the pulp in an aqueous suspension with elemental chlorine in solution in the aqueous phase. This operation constitutes the first stage in almost all wood pulp bleaching processes. Chlorine dioxide is sometimes admixed with the chlorine in this first stage and sometimes it replaces the chlorine.

Chlorination of the unbleached pulp so changes the ligneous impurities that they become, in part, soluble in water, while, of the proportion not readily soluble in water, a part is soluble in alkaline solutions such as dilute solutions of sodium hydroxide, sodium sulphite or ammonia. Pulps which have been treated to render the ligneous impurities soluble in water and dilute alkali, in particular treated with treating agents such as chlorine, chlorine dioxide and the oxides of nitrogen are referred to generally as pretreated pulp and after the pretreated pulp has been washed with water the pulp is extracted with a warm or hot solution of an alkali such as sodium hydroxide to effect removal of impurities insoluble in water alone. Extraction of the pretreated wood pulp with sodium hydroxide is generally conducted at a 10 to 14 percent consistency, at 40° to 70° C. with a retention time of 60 to 120 minutes.

Following the extraction of the pretreated pulp with sodium hydroxide and subsequent washing of the pulp the extracted pulp is oxidized with chlorine dioxide generally at a consistency of 6 to 15 percent and at a temperature from 65°–75° C. at a retention time from 3 to 5 hours.

These three stages are present in almost all multistage bleaching processes although many variations with regard to the stages are possible. For instance pulps made with certain species of wood makes a treatment with sodium or calcium hypochloride desirable between the extraction with sodium hydroxide and the chlorine dioxide treatment. Further, with kraft pulps the chlorine dioxide treatment is usually repeated, an extraction stage being interposed between the two chlorine dioxide oxidation stages.

Regardless of the number of stages as aforesaid the three treatments of the pulp are carried out in slurry form at consistencies varying from 3 to 15 percent and at times varying from 30 minutes to about 5 hours and at temperatures ranging from ambient to about 75° C. Due to the low consistency of the wood pulp being treated with the reagent in the aforesaid multistage bleaching process rates of reaction are slow and retention times in each stage are therefore long. This results in large equipment, large quantities of material in process, difficulty of control because of large time lag and waste chemicals consumed in secondary actions which contribute nothing to the overall multistage bleaching process. As set forth in applicant's Canadian Pat. Nos. 733,012, 752,864, 787,810 and 799,875, applicants have found that by conducting the treatment of the wood pulp with, e.g. chlorine, chlorine dioxide or ammonia at a high pulp consistency in the range from about 15 to 60 percent, by comminuting the high-consistency pulps into porous aggregates accessible to gas and that by treating the pulp with gaseous reagent instead of aqueous solutions of said reagents reaction times can be very much reduced, chemical usage can be reduced and the bleached pulp yield can be increased.

In particular, in Canadian Pat. Nos. 787,810 and 799,875 there is disclosed a process for the treatment of wood pulp which comprises continuously passing the pulp in the form of a comminuted moist fluff at a consistency suitably from 20 to 60 percent through a first zone of an atmosphere containing chlorine in an amount in excess of the potential amount of chlorine which will react with the pulp, limiting the residence time of the fluffed pulp within the first zone to such an extent that less than the potential amount of said chlorine, suitably 50–85 percent of the potential amount of the chlorine is acquired by the fluffed pulp, the residence time suitably being of the order of 20 seconds to 5 minutes and continuously passing the fluffed pulp including the acquired chlorine through a second zone of an essentially chlorine-free atmosphere so as to allow the unreacted amount of acquired chlorine to be removed from the fluffed pulp. The potential amount of chlorine as defined in those applications and as defined herein is the total amount of chlorine which will react with the lignin and other encrustants in the wood pulp as determined by accepted test methods.

In Canadian Pat. No. 752,864 there is disclosed a process for the ammonia extraction of pretreated wood pulp, i.e. wood pulp which has been pretreated with agents such as chlorine, chlorine dioxide and the oxides of nitrogen which process includes exposing a comminuted fluffed pretreated pulp at a consistency from between 15 and 60 percent to an atmosphere comprising gaseous ammonia at a temperature of about 60°–100° C. for a retention time of about 1 to 30 minutes.

Finally in Canadian Pat. No. 733,012 there is disclosed a process for treating unbleached or partially bleached wood pulp which comprises exposing comminuted fluffed wood pulp at a consistency of 30–40 percent to chlorine dioxide gas diluted with an inert gaseous diluent to a partial pressure of chlorine dioxide of not more than 100 mm. of mercury for a period of 5 to 30 minutes at a temperature from 65°–100° C. while controlling the pH range of the mixture so that the final pH is in the range from 3.5 to 6.5. **Thus, the reaction of chlorine dioxide with lignin produces strong acids as byproducts which tends to depress the pH to low levels and thus reduces the effectiveness of chlorine dioxide as a bleaching agent and it is preferred as set forth in this patent to incorporate a buffering agent such as a mild alkali or alkali metal salt of a weak acid into the pulp before contact with the chlorine dioxide gas.**

Applicants have now found according to the present invention that in order to realize fully the advantages of the gas phase reaction in the aforesaid multistage bleaching of cellulosic fibrous pulp the comminution of the pulp to produce the fluffed pulp must be of a specific nature so as to produce fragments which independent of their size are of low density, of porous structure throughout and substantially free from any highly compressed portions, i.e. compacted fiber bundles. Only when this form of comminuted pulp is achieved can the gaseous reactants reach all parts of the comminuted pulp fragments and thus ensure that the reaction of the gaseous reagent with the fluffed pulp proceeds rapidly and uniformly.

Existing apparatus for carrying out the comminution of the high-consistency cellulosic fibrous pulp to form a fluffed pulp either (*a*) support the pulp to be comminuted on a stationary member and the material is subjected to the action of moving members which move past and in close proximity to the stationary members thereby comminuting the material primarily by shear or (*b*) entrain the pulp to be comminuted between two sets of members one or both of which may be moving in close juxtaposition to one another and between which the pulp is subjected to shear. With both types of apparatus the pulp in addition to being subjected to shear is also subjected to some measure of localized very high pressure due to the small clearances between the shearing members. This compressive action is deleterious since at least a portion of the comminuted cellulosic pulp is highly compacted, i.e. in the form of highly compacted fiber bundles and thereby impervious to the gaseous reagent and is also difficult to redisperse in water.

According to the present invention therefore there is provided in the treatment of a fibrous cellulosic pulp in which said pulp is contacted in a fluffed form at a high consistency more than 15 percent with a gaseous reagent, the improvement in which said pulp at said consistency and prior to said contacting with said gaseous reagent is comminuted so as to have a low density substantially uncompacted porous fluffed structure.

According to a particularly preferred embodiment of the present invention there is provided in the multistage bleaching of a cellulosic fibrous pulp in which the pulp, in at least one stage, is contacted in a fluffed form at a consistency of more than 15 percent with a gaseous reagent the improvement in which the pulp at said consistency and prior to said contact with said gaseous reagent is comminuted sc as to have a low density substantially uncompacted porous fluffed structure.

Thus, to obtain the comminuted cellulosic fibrous pulp for use in the multistage bleaching process in accordance with the present invention the cellulosic fibrous pulp, in particular wood pulp, is passed at a consistency of more than 15 percent, in particular at a consistency between 15 and 60 percent if necessary having previously been dewatered to this consistency to a comminuting apparatus, as opposed to the conventional disc or hammer mils, in which comminuting apparatus the high-consistency pulp is unsupported and is broken up by contact with radial spaced breaker arms attached to a rotary shaft without any substantial local compression of the pulp and thus formation of compacted fiber bundles.

The present invention also provides an apparatus for comminuting a cellulosic fibrous pulp, such as wood pulp, to form a substantially uncompacted porous pulp having a low density here designated as fluffed pulp comprising a horizontal cylindrical housing, a shaft rotatably mounted substantially axially of said housing said shaft having radially extending therefrom a plurality of circumferentially and longitudinally spaced breaker members, terminating short of said housing to leave a space therebetween, inlet means for introducing said pulp into said housing adjacent the top thereof and outlet means for removal of comminuted fluffed pulp adjacent the bottom thereof. The inlet means suitably comprises a spout extending substantially the full length of the housing to facilitate the entry of high-consistency pulp under gravity to all parts of the housing and further the outlet means suitably comprises a plurality of longitudinally spaced slots extending circumferentially around the bottom portion of the housing the width of the slots being suitably adjustable by means of a sleeve member located adjacent the bottom of the housing, the sleeve member being adapted to move longitudinally of said housing and having a plurality of longitudinally spaced slots therein arranged to cooperate with the slots in the housing.

The improved fluffed pulp of the present invention may be used in any of the stages of the multistage bleaching process for the production of a bleached fibrous cellulosic pulp using a high-consistency pulp of at least 15 percent consistency and a gaseous reagent. In particular the pulp may be used in the initial treatment of the washed pulp from the cooking stage of the kraft, soda or sulphite process in which the pulp is contacted at a consistency of at least 15 percent with gaseous chlorine or gaseous chlorine dioxide or a mixture thereof.

Thus, in a particular aspect of the present invention there is provided in the multistage bleaching of a cellulosic fibrous pulp in which said pulp is contacted in a fluffed form at a consistency of more than 15 percent and suitably 15–60 percent which gaseous chlorine, the improvement in which the pulp at said consistency and prior to contacting with the gaseous reagent is comminuted so as to have a low density substantially uncompacted porous fluffed structure.

In particular, the present invention provides in said chlorination process continuously passing the fluffed pulp to a first zone in which it is contacted with an atmosphere containing excess chlorine, limiting the residence time of said fluffed pulp in said first zone such that less than the potential amount of chlorine is acquired by the fluffed pulp and continuously passing the fluffed pulp including said acquired chlorine through a second zone to allow unreacted chlorine to react with said fluffed pulp. Thus, the wood pulp at a consistency of 15–50 percent is first comminuted according to the process of the present invention into a dispersion of fibers and fiber aggregates and the wood pulp so obtained in the form of moist comminuted substantially uncompacted fluff is continuously passed through a zone of an atmosphere containing an excess of chlorine gas or chlorine gas diluted with air, the residence time in the zone being limited to such an extent that less than the potential amount of chlorine is acquired by the fluffed pulp, the residence time usually being of the order of 20 seconds to 5 minutes and the chlorine acquired by the fluffed pulp being usually from 50 to 85 percent of the potential amount of chlorine. The fluffed pulp including the chlorine which it has acquired in the first zone is then continuously passed through another zone where unreacted chlorine accompanying the fluffed pulp is removed from the vicinity of the pulp by a gentle stream of air to produce a pretreated wood pulp. The pretreated pulp is then suitably washed, extracted with an alkaline reagent, the extracted pulp washed, oxidized with chlorine dioxide and washed again. To obtain a fully bleached kraft or soda pulp the so-washed semibleached pulp may be extracted with an alkaline reagent, washed once more, oxidized with chlorine dioxide and finally washed.

When chlorine dioxide is used in the multistage bleaching process for the pretreatment of the washed high-consistency cooked wood pulp usually from the digester stage of the kraft, soda or sulfite process, the washed wood pulp in the form of a moist fluffed pulp at a consistency of 20–60 percent is treated with chlorine dioxide diluted with a nonreactive gas such as air, nitrogen or steam at a retention time generally of the order of 20 seconds to 60 minutes at a temperature which usually varies between 15° and 100° C. Subsequent to the chlorine dioxide pretreatment stage the pulp is washed, treated with an alkaline reagent to effect extraction thereof, washed, treated by a chlorine dioxide oxidation, washed and treated by a further alkaline extraction and finally washed and treated by a chlorine dioxide oxidation. All the chlorine dioxide oxidations in said multistage bleaching process may be conducted using the comminuted pulp according to the present invention.

In a further embodiment of the present invention the pretreated fibrous cellulose is comminuted according to the present invention and extracted by contact with a gaseous alkaline reagent, in particular ammonia, suitably at a temperature of 60°–100° C. Thus, in a particular aspect of the present invention a pretreated fluffed wood pulp at a consistency between 15 and 60 percent is extracted by heating to a temperature of about 60°–100° C., exposing the heated pulp to an atmosphere comprising gaseous ammonia for a reaction time of about 1–30 minutes and maintaining the reaction temperature during said contact in the range 60°–100° C. Thus, the washed pretreated pulp is comminuted into fiber aggregates generally of a consistency between 15 and 40 percent, the fiber aggregates preheated to a temperature generally in the range 60°–100° C., the preheated fiber aggregates exposed to an atmosphere comprising ammonia diluted with steam, air, nitrogen, or other nonreactive gas for a reaction time generally of the order of about 1–30 minutes. Subsequent to the reaction with ammonia the treated pulp is washed, oxidized with chlorine dioxide, washed, treated with an alkaline reagent, washed, treated with chlorine dioxide and further washed.

In the chlorine dioxide oxidation of the pulp subsequent to the alkaline extraction stage of the pretreated pulp the contact time usually ranges from 5 to 45 minutes and the temperature suitably in the range 65°–100° C. Further, to allow for the acid substances formed by the treatment of the alkaline extracted pulp with the chlorine dioxide the pH of the mixture is controlled so that the final pH is suitably in the range 3.5–6.5 usually by the addition of an alkaline agent to the pulp.

Thus, according to another embodiment of the present invention there is provided in the multistage bleaching of a cellulosic fibrous pulp a process which comprises contacting an

alkali-extracted fluffed pretreated wood pulp at a consistency of 20–40 percent with a mixture of chlorine dioxide gas and an inert diluent gas such that the partial pressure of the chlorine dioxide gas is not more than 100 mm. of mercury for a period of 5–45 minutes at a temperature of about 65°–100° C. in the presence of a buffering agent to maintain the pH of the pulp during reaction in the range 3.5–6.5. Subsequently, the pulp may be washed.

When in the aforesaid multistage bleaching process the chlorine dioxide is used to further delignify a partially delignified wood pulp the chlorine dioxide treated pulp is suitably subsequently washed, extracted with an alkaline reagent, washed again, further treated with chlorine dioxide or another oxidizing agent and finally washed.

It will be readily obvious that the pretreatment of the cellulosic fibrous pulp with chlorine or chlorine dioxide, its subsequent extraction with ammonia and its subsequent oxidation with chlorine dioxide and extraction with ammonia may all be conducted according to the process of the present invention in the multistage bleaching process.

Thus, in a particular preferred embodiment of the present invention there is provided in the multistage bleaching of fibrous cellulosic pulp the steps of washing cooked fibrous cellulosic pulp, dewatering the pulp to a consistency of 15–60 percent, comminuting the pulp so as to have a low-density substantially uncompacted porous fluffed structure, continuously passing the fluffed pulp to a zone having an atmosphere containing an excess of chlorine gas or chlorine gas diluted with air, limiting the residence time within the zone to such an extent that less than the potential amount of chlorine is acquired by the fluffed pulp, continuously passing the fluffed pulp including the chlorine which has been acquired by the fluffed pulp through a second zone of an essentially chlorine-free atmosphere, washing the pretreated pulp, dewatering the pretreated pulp, to a consistency of 15–40 percent, comminuting the washed pulp at said consistency so as to have a low-density, substantially uncompacted porous fluffed structure, preheating the fluffed pulp to a temperature in the range 60°–100° C., exposing said preheated pulp to an atmosphere comprising gaseous ammonia diluted with steam, air, nitrogen or another inert gas for a reaction time generally of the order of 1–30 minutes while maintaining the temperature during the reaction time in the range 60°–100° C., washing the pulp, dewatering the washed pulp to a consistency of 20–40 percent comminuting the pulp so as to have a low-density substantially uncompacted porous fluff structure exposing the fluffed pulp to chlorine dioxide gas diluted with an inert diluent gas to a partial pressure of chlorine dioxide not more than 100 mm. of mercury for a period from 5 to 45 minutes at a temperature from 65°–100° C., said pulp containing an alkaline agent thereby to control the pH of the mixture so that the final pH is in the range 3.5–6.5 and washing the oxidized pulp.

The order of treatments may, of course, be varied, a conventional hypochlorite treatment may be interposed between the ammonia and chlorine dioxide treatments, the sequence may be terminated after the first chlorine dioxide stage in the case of easily bleached pulp such as sulfite pulp or alternatively in the case of kraft pulp the sequence may likewise be terminated after the first chlorine dioxide stage to provide semibleached pulp.

The present invention will be further illustrated by way of the accompanying drawings in which

FIG. 1 is a side elevation partially broken away of a comminuting device for producing the fluffed pulp as required in the process of the present invention;

FIG. 2 is a section taken along the lines 2—2 in FIG. 1;

FIG. 3 is a diagrammatic flow sheet for effecting the multistage bleaching process according to a preferred embodiment of the present invention;

FIG. 4 is a vertical diagrammatic sectional detail of the reactor for pretreating the pulp with chlorine gas; and

FIG. 5 is a vertical diagrammatic detail of the reactor for oxidizing the extracted pretreated pulp with chlorine dioxide.

FIGS. 6A and 7A are photographs of bleached low-density uncompacted pulp which has been comminuted and fluffed according to the invention before bleaching.

FIGS. 6B and 7B are photographs of bleached pulp which has been comminuted and fluffed by conventional procedures before bleaching.

Referring to FIGS. 1 and 2 the comminuting device comprises a drum housing 1 having rotatably mounted axially thereof, a shaft 2 driven by an electric motor (not shown). Mounted on the shaft 2 are a plurality of circumferentially and longitudinally spaced breaker members 3 which are suitably in the form of spikes which may be straight or curved in the direction of motion or have straight and curved portions. The ends of the spikes 3 may be suitably pointed to enhance the breaking action upon the high-consistency wood pulp introduced into the housing 1. The housing 1 is closed at each end by means of end walls containing bearings (not shown) to support the shaft 2. The housing 1 has a plurality of longitudinally spaced circumferentially extending slots 4 covering approximately the lower half of the circumference thereof. In contact with the inner surface of the housing 1 and covering an arc at least as great as that of the slots 4 is a slidable sleeve 5 having slots 6 therein which are about as wide as the slots 4 in the housing 1 with the same center to center spacing. A threaded rod 7 protruding through one of the end walls of the housing 1 and fitted with a threaded nut is present to move the sleeve 5 longitudinally with respect to said housing 1 to alter the relative positions of the slots 4 and 6 thereby vary the width of the slots communicating the interior with the exterior of the housing 1.

The housing 1 has an opening at the top to receive a feed spout 8 which preferably extends substantially the full length of the housing 1 and is also preferably inclined to the vertical to prevent comminuted pulp being flung back from the interior of the housing any distance up the spout 8.

The dimensions of the comminuting device and of all its parts will vary with the throughput of pulp required. To increase capacity it is preferable to increase the length of the device rather than the diameter. The diameter of the housing 1 may conveniently vary from about 6 to 24 inches and its length may suitably vary from a few inches to several feet. The diameter of the spikes 3 is preferably kept as small as possible having regard to their mechanical strength and rigidity and will be suitably between three-sixteenths and three-fourths of an inch and the length of the spikes 3 will depend upon the maximum size of fragments desired and will be such as to provide a clearance between their tips and the inside periphery of the sleeve 5. This clearance will normally be between one-eighth inch and an inch. The width of the slots 4 and 6 in the housing 1 of the sleeve 5 depends upon the maximum size of the fragments desired but will seldom exceed an inch. The width of the lands or solid portion between the slots 4 and 6 is not critical but is preferably a minimum commensurate with the structural strength of the device to permit maximum facility of discharge of comminuted fluffed pulp. Since the minimum effective slot width is determined by the position of the sleeve 5 with respect to the housing 1 the width of the slots 4 and 6 themselves can be substantially larger than the maximum size of the fluffed comminuted pulp desired but it will seldom be less than one-fourth of an inch. The exact location and disposition of the spikes 3 on the shaft 2 are not critical and are subject to wide variation. However, a preferred arrangement is one in which the spikes 3 rotating in adjacent planes are spaced not more than the maximum size of pulp fragment desired. Obviously, the arrangement of the spikes 3 should be such that the spike-shaft assembly is dynamically balanced. Although the shaft 2 has been shown in the drawings as concentric with the housing 1 this is not critical and the centerline of the shaft 2 need not coincide with the centerline of the housing 1. If it does not, the centerline of the shaft 2 is preferably located on the vertical centerline and below the horizontal centerline of the housing 1.

The speed of rotation of the shaft 2 and spikes 3 should be such that the linear peripheral speed of the tips of the spikes 3 will be sufficient to effect the desired comminution action which will depend on the pulp being treated but will usually be in the range 1,500 feet per minute to about 6,000 feet per minute.

In operation the pulp to be comminuted is fed via the spout 8 in the form of a continuous web, cakes, sheets or large fragments in the housing 1. As the pulp enters the housing 1 although unsupported, its inertia is such that only a small portion thereof can accelerate sufficiently rapidly to be carried along at the speed of the tips of the spikes 3. The spikes 3 therefore tear through the pulp carrying forward only a small quantity at their own speed. Although by virtue of this same inertia some compaction of the pulp occurs at the point of impact of the spikes 3 since the pulp is unsupported this compaction is slight and unobjectionable. Fragments of pulp larger than the maximum desired size which may escape the first impact of the spikes 3 will fall to the bottom of the housing 1 where they will subsequently be impacted by the same or adjacent spikes and be further fragmented until they are reduced to a size small enough to drop through the slots 4 in the housing 1 and be discharged from the device. The comminuting action on the pulp is extremely important in the process of the present invention and the fragments produced must be of low density and of uniformly porous structure and have undergone as little compaction as possible. In the prior apparatus the pulp being supported on a fixed member at the moment of comminution or otherwise squeezed between coacting members is subjected to undesirable compaction and is unsuitable for uniform and rapid reaction with the gaseous reagent.

Referring now to FIG. 3, cooked wood pulp suitably obtained from the digestion stages of the kraft process is washed and dewatered to a consistency of 15–40 percent in particular about 30 percent by pressing and is fed to a comminuting device **10** suitably operating as described with reference to FIGS. 1 and 2. From the device **10** the fluffed pulp is fed to a reactor **11**, where it is contacted with chlorine gas entering through line **12** for a period of about 60 seconds at ambient temperature and the chlorine gas present in the pulp removed therefrom by air introduced through line **13** as will be more particularly described hereinafter.

The chlorinated i.e. pretreated wood pulp is then discharged from the reactor **11** to a dilution tank **14** in which it is diluted with water to a consistency suitably in the range 0.5 to 3 percent and pumped by pump **15** to a drum washer **16**. Washed pulp leaves the washer **16** in the form of a thick web which is pressed between press rolls **17** to a consistency in the range 15 to 30 percent particularly about 20 percent and then passed to a reactor **19** via a conventional coarse shredder **17***a* and a comminuting device **18** similar to the comminuting device **10**.

In the reactor **19** the fluffed pulp is contacted with gaseous ammonia diluted with steam entering through line **21**. The gaseous ammonia being suitably added in an amount 0.5 to 2.0 percent of the dry weight of the pulp and steam entering through line **20** to preheat the pulp, the total amount of steam being sufficient to heat the pulp, to between 80° and 100° C. The contact time with the gaseous ammonia is suitably about 60 seconds. The extracted pulp is then passed to a dilution tank **22** in which it is diluted with water to a consistency of 0.5 to 3 percent and from the tank **22** pumped by pump **23** to a drum washer **24** similar to the drum washer **16**. The pulp web obtained from the washer **24** passes to press rolls **25** during which an alkaline buffering agent such as sodium carbonate in powder or solution form is added to the pulp through line **26** in an amount of the order of 1 to 1.5 percent by weight which is sufficient to ensure that at the end of the subsequent chlorine dioxide treatment in reactor **29** the pH of the pulp does not fall below 3.5. The press rolls **25** dewater the web to a consistency to be in the range 20–40 percent particularly 30 percent and the buffered pulp passes to the reactor **29** via a conventional coarse shredder **27** and a comminuting device **28** similar to comminuting device **10**.

In the reactor **29** the pulp is treated with chlorine dioxide gas diluted with steam and/or air entering through line **31** in an amount of 0.5 to 1.5 percent by weight of the dry pulp, steam entering through line **30** in an amount sufficient to heat the pulp to a temperature in the range of from 65° to 100° C., air entering through line **30** in an amount sufficient to ensure that the partial pressure of chlorine dioxide gas at no time exceeds 100 mm. of mercury. Contact time between the chlorine dioxide gas and the pulp in reactor **29** is suitably 5 to 45 minutes. At the bottom of the reactor **29** the treated pulp is diluted with water entering through line **33** to a consistency of 0.5 to 3 percent and pumped by pump **34** to a drum washer **35**. The washed web from the washer **35** is pressed by press rolls **36** to a consistency of 15 to 30 percent and the high-consistency web passes to a reactor **39** via coarse shredder **37** and comminuting device **38** similar to device **10**.

In the reactor **39** which is similar to the reactor **19** the pulp is treated with gaseous ammonia diluted with steam entering through line **41**, the gaseous ammonia being added in an amount from 0.1 to 0.5 percent dry weight of the pulp and steam entering through line **40** to preheat the pulp, the total amount of steam being sufficient to heat the pulp, to a temperature of 80° to 100° C. Contact time is again about 60 seconds. The extracted pulp passes from the reactor **39** to a dilution tank **42** where it is diluted to a consistency in the range 0.5 to 3 percent and pumped by pump **43** to a drum washer **44** from where the washed pulp therefor of a web is dewatered by press rolls **44***a* to a consistency of 20 to 40 percent and to a reactor **47** via a conventional coarse shredder **45** and comminuting device **46** such as to the device **10**.

In the reactor **47** the pulp is contacted with chlorine dioxide gas diluted with steam and/or air entering through line **49** in an amount from 0.2 to 0.5 percent dry weight of the pulp and steam entering through line **48**, air entering through line **49** under similar conditions as in reactor **29**. The fully bleached pulp is diluted with water entering the bottom of the reactor **47** via line **51** to a consistency in the range 0.5 to 3 percent and pumped by pump **52** to a drum washer **53** from where it is discharged for subsequent drying or further processing.

The reactor **11** is particularly illustrated in FIG. 4. The fluffed pulp from the comminuting device **10** is fed through the inlet **100** into a vertical cylindrical vessel **101**. The pretreated pulp discharges into the dilution tank **14** from the bottom end **102** of said vessel **101** which bottom end **102** is of slightly smaller diameter. The lower edge of the end **102** is in the form of a short frustoconical section **111** to impede free discharge of the pretreated pulp and induce a measure of compaction. Discharge of the pulp from said bottom end **102** is regulated by means of a screw **103** mounted at the lower end of a hollow rotatable shaft **104** extending axially down the vessel **101** and driven by a variable speed electric motor **105**. The shaft **104** is encased in a tube **106**, chlorine being passed through line **12** down the tube **106** and into the pulp through perforations **107** and air being passed into the pulp from line **13** through hollow shaft **104** and radially extending tubes **108**. The lines **12** and **13** are connected to the shaft **104** and the tube **106** (when rotatable with the shaft **104**) by means of rotary joints (not shown). Chlorine gas may also be supplied from line **12** to the pulp in the vessel **101** via a perforated ring **109** via connecting lines (not shown). The chlorine gas thus supplied to the pulp in the vessel **101** due to its high density displaces air in the pulp and rises in the vessel **101** where it is sensed by a sensing device **110** which controls a chlorine gas feed valve (not shown) in line **12** so as to maintain the chlorine concentration at the level of the device **110** at a predetermined maximum value. Chlorine gas acquired by the pulp in the vessel **101** is subsequently washed out, as the pulp descends through the vessel, by the air.

The level of the pulp in the vessel **101** is sensed by a sensing device **112**, such as a sonic detector, which maintains the level constant by controlling the speed of the motor **105**.

In operation the fluffed pulp is fed to the vessel **101** of the reactor **11** via inlet **100** the level of the pulp in the vessel being sensed by sensing device **112**. The rate of feed of fluffed pulp

to the reactor 11 and dimensions of the reactor 11 are proportioned to provide the required retention time of the pulp in the reactor. The chlorine gas entering the reactor 11 through the perforations 107 and 109 substantially fills the reactor to a level governed by the sensing device 110 and because of its high density the chlorine gas tends to remain in the reactor and not rise and escape from the top thereof. The pulp in descending through the pool of excess chlorine gas so formed adsorbs a quantity of chlorine determined by its lignin content and its time of passage through the reactor 11. Air introduced into the reactor 11 via perforated tubes 108 flushes from the pulp unreacted excess chlorine held by the pulp and thus minimizes wastage. Part of the air flows upwards and is vented through outlet 113. During its passage up the reactor 11 this air entrains chlorine gas above the level controlled by device 110 but the entrained chlorine gas meets descending fresh pulp which quickly reacts with it thus stripping the chlorine from the air and preventing escape of chlorine gas from the vent 113. The remainder of the air passes out with the pretreated pulp at the bottom 102 of the vessel 101, the frustoconical edge 111 ensuring that the majority of the air flows upwardly in the vessel 101 by impeding free discharge of the pulp and inducing a measure of compaction in the pulp.

The reactors 19 and 39 are similar in construction to reactor 11 except that the sensing device 110 is not required as in these reactions a small amount of ammonia is metered into the reactors, dependent on the demands, and not an excess of gas as required in reactor 11. Further the air inlet 12 and the perforated tubes 108 are not necessary as flushing air is not required and the shaft 104 may be solid. Finally, the gas perforations 107 and 109 may be higher in the reactor so as to obtain contact with the pulp earlier in its descent through the vessel 101 and alternatively the addition of steam and ammonia gas to the reactor may be split so as to add steam along first at a high level in the reactor so as to preheat the pulp and the mixture of ammonia gas and steam at a lower level.

Turning to FIG. 5 in the reactors 29 and 47 longer reaction times are desirable than in reactors 11, 19 and 39. The upper part of the reactors is similar to that in FIG. 4 and in particular a vertical cylindrical vessel 120 has a pulp inlet 121, a lower pulp outlet 122 of reduced diameter and a frustoconical lower edge 123. The passage of the pulp through the vessel is regulated by a screw 124 located at the lower end of a hollow rotatable shaft 125 driven by a variable speed electric motor 126 controlled by a pulp level sensing device 127. A mixture of chlorine dioxide gas, steam and air is introduced via line 128 into the hollow shaft 125 and into the pulp via perforations 129. Also the mixture is introduced from the inlet 128 via perforations 130 in a hollow ring. A temperature-sensing device 137 is also present.

The aforesaid vessel 120 of the reactor 29 and 47 serves to contact the pulp and the chlorine dioxide and raise its temperature to the desired level. The pulp and absorbed chlorine dioxide is then discharged to the lower portion 132 of the reactor which is dimensioned to provide the desired retention time to permit completing the reaction between the absorbed chlorine dioxide and the pulp. The pulp accumulates in the lower portion 132 until a level 133 is reached which is sensed by level controller 134 which controls the speed of pump 34 (or 52) so as to hold a constant level. Water is added via inlet 33 (or 51) up to the level 135 which is sensed by level sensor 136 which controls the admission rate. Sensors 134 and 136 and the speed control of the pump 34 are similarly interlocked with a consistency controller (not shown) following pump 34 to maintain the pulp in the desired consistency. Temperature controller 139 regulates the admission of steam through line 138 to maintain the temperature of the pulp in the lower portion 132.

It will be realized that the number of stages in the aforesaid bleaching process may be varied and also the sequence of treatment of the pulp with the various gaseous reagents. Thus, for sulphite pulp the bleaching may be terminated at the washer 35 and for a kraft pulp termination at the washer 35 yields a semibleached pulp. In full bleaching of kraft pulps it may be desirable to interpose a conventional hypochlorite bleaching stage between the washer 35 and the shredder 37. The press rolls may be replaced by screw or disc presses or other dewatering devices and the coarse shredders omitted.

The present invention will be further illustrated by way of the following examples in which the conditions used and results obtained in bleaching wood pulp by the conventional low-consistency gas-phase techniques and the high-consistency gas-phase technique according to the present invention using the same bleaching chemicals in the same sequence of stages is given.

EXAMPLE I

A portion of an unbleached kraft pulp from coniferous wood characterized by a Roe chlorine number 5.4, Kappa No. 34.1 and 0.5 percent cupriethylendiamine viscosity 34.7, was bleached in a five-stage sequence by the high-consistency gas-phase technique. Another portion was bleached in a five-stage sequence using the conventional low-consistency technique. Table I shows the conditions and results.

TABLE I

Operating Conditions	High Consistency	Low Consistency
Chlorination		
% Cl_2	3.7	6.5
Temp. °C.	35	25
% Consistency	30	3.0
Time (min.)	1	60
1st Extraction		
% NH_3	1.25	—
% NaOH	—	3.0
Temp. °C.	100	70
% Consistency	20	10
Time (min.)	1	90
1st Chlorine Dioxide		
% ClO_2	1.0	1.20
Temp. °C.	85	70
% Consistency	30	12
Time (min.)	30	180
2nd Extraction		
% NH_3	0.5	—
% NaOH	—	1.0
Temp. °C.	100	70
% Consistency	20	10
Time (min.)	1	90
2nd Chlorine Dioxide		
% ClO_2	0.25	0.35
Temp. °C.	85	70
% Consistency	30	12
Time (min.)	30	180
Results		
Pulp Brightness—% Elrepho	91.2	90.2
Shrinkage %	5.3	8.4
CED Viscosity cps.	28.9	20.9
Pulp properties at 300 CSF:		
Burst Factor	109.8	102.8
Breaking Length (m.)	13,325	12,500
Tear Factor	100	95
Beating Time—Revs. PFI mill	10,900	11,300

EXAMPLE II

A portion of an unbleached kraft pulp from deciduous wood characterized by a Roe chlorine number 1.8, Kappa No. 15.5 and 0.5 percent cupriethylenediamine viscosity 35.1, was bleached in a five-stage sequence by the high-consistency gas-phase technique. Another portion was bleached in a five-stage sequence using the conventional low-consistency technique. Table II shows conditions and results.

TABLE II

Operating Conditions	High Consistency	Low Consistency
Chlorination		
% Cl_2	1.3	3.2
Temp. °C.	25	25
% Consistency	30	3.0
Time (min.)	1	45
1st Extraction		
% NH_3	1.01	—
% NaOH	—	2.0
Temp. °C.	100	70
% Consistency	20	10
Time (min.)	1	90
1st Chlorine Dioxide		
% ClO_2	0.80	1.00
Temp. °C.	85	70
% Consistency	30	12
Time (min.)	30	180
2nd Extraction		
% NH_3	0.3	—
% NaOH	—	1.0
Temp. °C.	100	70
% Consistency	20	10
Time (min.)	1	90
2nd Chlorine Dioxide		
% ClO_2	0.25	0.40
Temp. °C.	85	70
% Consistency	30	12
Time (min.)	30	180
Results		
Pulp Brightness—% Elrepho	91.8	90.4
Shrinkage %	3.7	4.8
CED Viscosity c.p.s.	28.2	19.7
Pulp Properties at 300 CSF:		
Burst Factor	59.0	62.2
Breaking Length (m.)	2,130	2,155
Tear Factor	83	80
Beating Time—Revs. PFI mill	8,850	11,300

EXAMPLE III

A portion of an unbleached sulfite pulp from coniferous wood characterized by a Roe chlorine number 6.2, Kappa No. 27.8 and 0.5 percent cupriethylenediamine viscosity 35.0, was bleached in a three-stage sequence by the high-consistency gas-phase technique. Another portion was bleached in a three-stage sequence using the conventional low-consistency technique. Table III shows conditions and results.

TABLE III

Operating Conditions	High Consistency	Low Consistency
Chlorination		
% Cl_2	4.4	6.2
Temp. °C.	28	25
% Consistency	30	3.0
Time (min.)	1	45
Extraction		
% NH_3	1.0	—
% NaOH	—	2.0
Temp. °C.	100	70
% Consistency	30	10
Time (min.)	1	90
Chlorine Dioxide		
% ClO_2	0.60	1.00
Temp. °C.	85	70
% Consistency	30	12
Time (min.)	30	180
Results		
Pulp Brightness—% Elrepho	92.8	91.9
Shrinkage %	5.6	7.5
CED Viscosity cps.	41.0	37.3
Properties at 300 CSF:		
Burst Factor	75.5	73.5
Breaking Length (m.)	10,750	10,500
Tear Factor	61	60
Beating Time—Revs. PFI mill	7,900	9,250

EXAMPLE IV

A portion of an unbleached kraft pulp from coniferous wood characterized by Roe chlorine number 3.3, Kappa No. 21.2 and cupriethylenediamine viscosity 21.3, was semibleached in three high-consistency gas-phase bleaching stages. Another portion of the same unbleached pulp was semibleached in three conventional low-consistency stages. Table IV shows the conditions and results.

TABLE IV

Operating Conditions	High Consistency	Low Consistency
Chlorination		
% CL_2	2.4	4.0
Temp. °C.	25	25
% Consistency	30	3.0
Time (min.)	1	60
Extraction		
% NH_3	1.0	—
% NaOH	—	2.0
% Consistency	20	10
Temp. °C.	100	70
Time (min.)	1	90
Chlorine Dioxide		
% ClO_2	0.90	1.0
Temp. °C.	85	70
% Consistency	30	12
Time (min.)	30	180
Results		
Pulp Brightness—% Elrepho	83.9	83.2
Shrinkage %	4.4	5.3
CED Viscosity cps.	19.2	17.2
Pulp Properties at 300 CSF:		
Burst Factor	99.5	96.0
Breaking Length (m.)	13,150	12,650
Tear Factor	101	98
Beating Time—(Valley Beater)	48	61

It is apparent from tables I, II, III and IV that for substantially the same bleached pulp brightness, chemical consumption is sharply reduced, yield of bleached pulp brightness, chemical consumption is sharply reduced, yield of bleached pulp is increased and substantially the same strength properties are obtained in sharply reduced beating time by the high-consistency gas-phase bleaching technique of the present invention.

EXAMPLE V

Two portions of an unbleached Kraft pulp from coniferous wood characterized by a Roe chlorine number 4.9 and a Kappa number 29.4 were separately bleached in a five-stage sequence by the high-consistency gas-phase technique. Prior to each bleaching stage the pulp was fluffed, one portion using the comminuting apparatus of FIGS. 1 and 2, and the other using a Sprout Waldron Disk Refiner MOdel 103 plate number 18034 at 0.030 in clearance. The pulp was comminuted at 30 percent consistency since the Disk Refiner tended to clog and jam at lower consistencies. The conditions and results obtained are given in table V.

TABLE V

Operating Conditions	Apparatus of the Present Invention	Sprout Waldron Disk Refiner
Chlorination		
% Cl_2	2.6	2.6
Temp. °C.	27	27
% Consistency	30	30
Time (min.)	1	1
1st Extraction		
% NH_3	1.01	1.02
Temp. °C.	100	100
% Consistency	30	30
Time (min.)	1	1
Results		
Kappa No.	6.1	8.2
1st Chlorine Dioxide		
% ClO_2	1.0	1.0
Temp. °C.	85	85
% Consistency	30	30
Time (min.)	6 and 30	6 and 30
Results		
Pulp Brightness % Elrepho		
at 6 min.	80.4	63.8
at 30 min.	83.7	76.8
2nd Extraction		
% NH_3	0.3	0.3
Temp. °C.	100	100
% Consistency	30	30
Time (min.)	1	1
2nd Chlorine Dioxide		
% ClO_2	0.25	0.25
Temp. °C.	85	85
% Consistency	30	30
Time (min.)	6 and 30	6 and 30
Results		
Pulp Brightness % Elrepho		
at 6 min.	89.7	85.8
at 30 min.	92.3	90.9

It will be seen from table V that the brightness of the pulp was higher and the Kappa number was lower for the pulp fluffed in the apparatus of the present invention. Further as will be seen from the photographs the pulp of FIG. 6A produced in the apparatus of the present invention is quite uniform after 6 minutes treatment with chlorine dioxide in comparison to the spotty, nonuniform pulp of FIG. 6B which is the pulp from the Disk Mill Refiner subjected to a similar chlorine dioxide treatment. FIG. 7A shows the washed pulp of FIG. 6A and FIG. 7B shows the pulp of FIG. 6B after washing. The dark spots in FIG. 7B contribute to lower pulp brightness. Since the dosage of chemical with both portions of pulp is the same the increase in brightness is directly attributable to the fluffing procedure of the present invention.

We claim:

1. In the treatment of a chemical cellulosic fibrous pulp in which said pulp is contacted in a fluffed form at a consistency of more than 15 percent with a gaseous bleaching agent, the improvement which comprises comminuting said pulp prior to said contacting with said gaseous bleaching agent by repeatedly contacting with said gaseous bleaching agent by repeatedly contacting said pulp, at said consistency and while unsupported, with radial spaced breaker arms extending from a rotating shaft whereby the resulting comminuted pulp has a low-density substantially uncompacted porous fluffed structure, continuously passing said fluffed pulp to a first zone in which it is contacted with an atmosphere containing chlorine in an amount in excess of the potential amount of chlorine which will react with said pulp, limiting the residence time in said first zone such that less than the potential amount of chlorine is acquired by said fluffed pulp and continuously passing said fluffed pulp including said acquired chlorine through a second zone of an essentially chlorine-free atmosphere to allow unreacted chlorine to react with the fluffed pulp, washing the pulp with water, dewatering the washed pulp to a consistency of more than 15 percent, extracting the thus-pretreated fluffed pulp by contact with a gaseous ammonia reagent, washing the pulp with water, contacting the alkaline-extracted fluffed pulp at a consistency of 20–40 percent with a mixture of chlorine dioxide gas and an inert diluent gas such that the partial pressure of the chlorine dioxide gas is not more than 100 mm. of mercury, for a period of 5 to 45 minutes at a temperature of about 65°–100° C. and controlling the pH of the pulp during the reaction in the range of 3.5 to 6.5 by the addition of an alkaline reagent, prior to treatment with the chlorine dioxide.

2. A process as claimed in claim 1 in which the pulp is dewatered to a consistency between 15 and 60 percent before comminution thereof.

3. A process as claimed in claim 1 in which the pulp is wood pulp.

4. A process as claimed in claim 3 in which the wood pulp is unbleached before being comminuted.

5. A process as claimed in claim 1 which comprises removing unreacted chlorine in said second zone from the pulp by means of passage of air therethrough.

6. A process as claimed in claim 1 in which the fluffed pulp in said first zone has a consistency of 15–60 percent.

7. A process as claimed in claim 1 in which the residence time in the first zone is from 20 seconds to 5 minutes, during which time from 50–85 percent of the potential amount of chlorine is acquired by the fluffed pulp.

8. A process as claimed in claim 1 in which the breaker arms have a linear peripheral speed in the range of 1,500 to 6,000 feet per minute.

9. A process as claimed in claim 1 in which the comminuted fluffed pulp, following treatment in the second zone, is heated to a temperature of about 60° to 100° C. and the preheated pulp is contacted with the gaseous ammonia reagent for a reaction time of about 1 to 30 minutes at a temperature of about 60°–100° C.

10. A process as claimed in claim 1 in which the gaseous ammonia reagent includes steam or a nonreactive gas as a diluent.

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