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BLEACHING PULP HAVING HIGH CONSISTENCY WITH OZONE HAVING MOISTURE CONTENT NEAR 100 %

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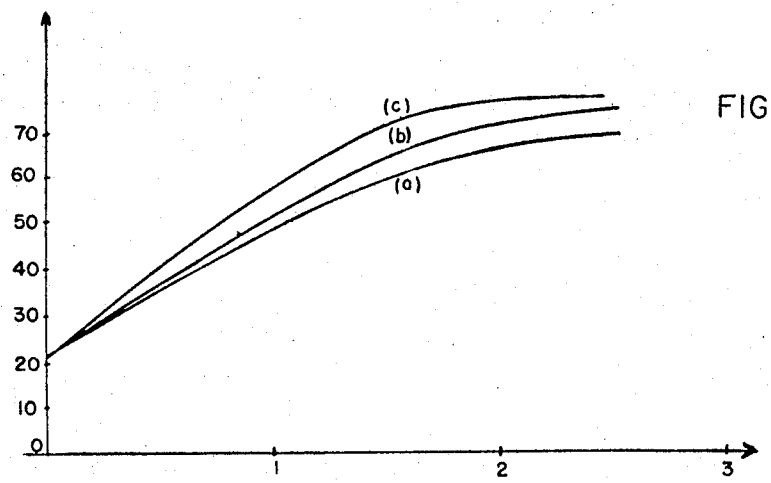

FIG. 1

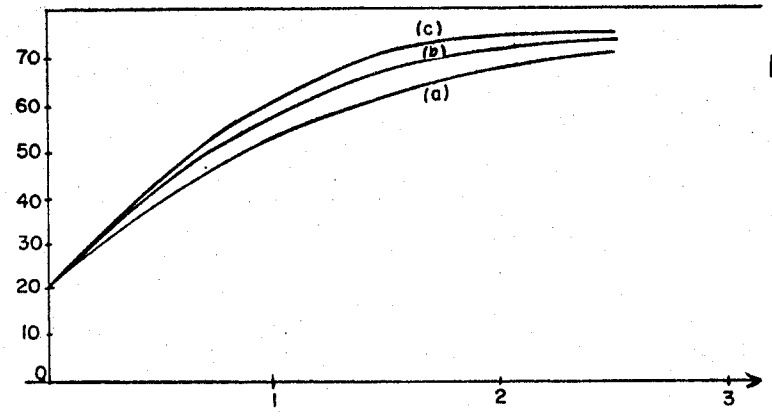

FIG. 2

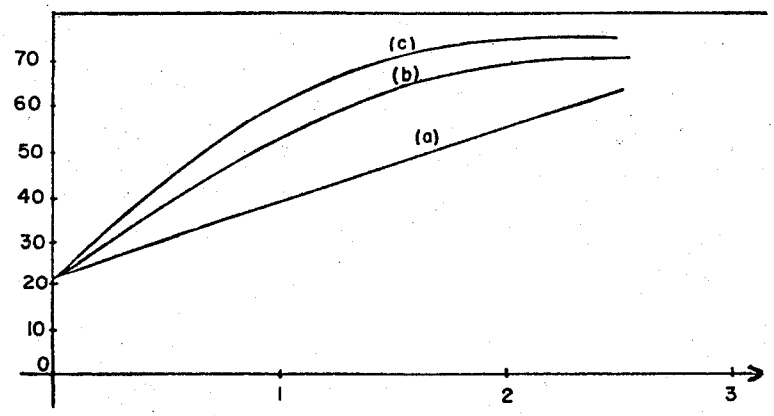

FIG. 3

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BLEACHING PULP HAVING HIGH CONSISTENCY WITH OZONE HAVING MOISTURE CONTENT NEAR 100%

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U.S. Cl. 162—65 8 Claims

ABSTRACT OF THE DISCLOSURE

A method of bleaching paper-making pulp which is an aqueous slurry having a dry consistency of 30–65% by passing a gaseous stream containing ozone which has a moisture content near 100% through the pulp.

The present invention relates to a method of bleaching paper pulp utilizing ozone. More particularly, it relates to the use of wetted ozonized air as a bleaching agent.

In classical processes, bleaching is effected on cellulosic pulps, in a combined way, with active products such as chlorine, chlorine dioxide, soda and sodium hypochlorite. But applied techniques are long and expensive as they need several treatment stages and extensive equipment.

It has been tried to bleach paper pulps by means of dry ozonized air. This method reduced corrosion problems and makes the working process easier. Moreover, since ozone is produced only by the action of an electric discharge upon air, the bleaching agent is continually available without any raw material stocking. But it has been noted that such a treatment gives rise to a very important pulp drying. This disadvantage is the more serious as, when starting from a dry gaseous flow, the humidity rate of the whole system varies progressively to the reaction between cellulosic material and ozonized air. So drying is more or less pronounced in the different parts of the pulp and it results in irregular non-homogeneous bleaching. It is not possible to stop this phenomenon by lengthening treatment time, since this results in a whiteness reversion. Moreover, the pulp becomes strongly degraded, especially at the points where drying is the most pronounced, and it shows characteristics incompatible with market requirements.

The present invention has for an object the provision of a bleaching process, very easy to carry out, and leading to an improved whiteness, keeping at the same time pulp quality.

Also, the invention provides for a given whiteness equal to the one of a classical bleaching, the improvement of pulp characteristics.

The applicants have found the above results are obtained by the action of an ozonized air flow saturated with moisture upon the pulp to be bleached. Indeed it has been established that, when the process is carried out with a wetted gaseous flow, the moisture rate of the system remains constant and optimal, contrary to what happens with dry ozonized air. There is neither local drying nor cellulose degradation and bleaching is homogeneous and regular.

In its most general form, the process according to the invention comprises passing a gaseous flow, coming from an ozonizer and titrating 2.5 to 18 mg. O_3/liter, preferably 4 to 16 mg./liter, into a saturator/moistener, then sending it as it escapes from the apparatus at a rate of 50 to 500 liter/hour, preferably 100 to 300 liter/hour

during a time of ½–2½ hours, preferably 1 to 2 hours, to a shredded paper pulp, with a dryness of 30–65%, having a pH near neutrality and maintained at a temperature of 20 to 30° C.

The moisture state of the gaseous flow is an essential element of the process according to the present invention. The ozonized air must have a relative moisture near 100%. In any case it is necessary that the moisture content be the highest possible in order to avoid any drying variation of the pulp in treatment and to give to bleaching its efficiency maximum.

The ozonized gaseous flow according to the invention may be constituted not only by air, as this is considered during this description, but also by oxygen.

Azone titre and gaseous rate may be selected in the present invention field wiht regard to the variables inherent to the used installation without being prejudicial to the obtained result: indeed experiment has shown that the important factor in this field is the weight of used ozone per time unit. For example a fairly similar whiteness will be obtained in carrying out the process during the same time: A gaseous flow at a rate of 300 l./hr., titrating 6.10 mg. O_3/l. (that is 1830 mg. O_3/hr.); a gaseous flow at a rate of 200 l./hr., titrating 9.30 mg. O_3/l. (that is 1860 mg. O_3/hr.).

Treatment time may vary in the limits of 30 minutes to 2 hours 30 minutes according to the conditions selected in the field in order to give a maximum treatment efficiency. This may easily be established with regard to the selected gaseous rate and/or ozone titre, so as to obtain the desired bleaching degree. For example, a whiteness, "Elrepho" of 60 may be obtained:

in 1 hr. with a gaseous rate of 300 l./hr. titrating 6.10 mg. O_3/l.;
in 1½ hr. with a gaseous rate of 100 l./hr. titrating 6.50 mg. O_3/l..

In the same way a whiteness "Elrepho" of 71 may be obtained:

in 1½ hr. with a gaseous rate of 200 l./hr. titrating 9.4 mg. O_3/l.;
in 2 hr. with a gaseous rate of 200 l./hr. titrating 7 mg. O_3/l.;
in 2½ hr. with a gaseous rate of 200 l./hr. titrating 4 mg. O_3/l.

The charts of FIGS. 1, 2 and 3 allow one to determine in an easy way gaseous flow rate, ozone titre and treatment time which may be chosen with regard to the desired result.

On these charts are plotted, as absicissa, the time in hours of ozonized air treatment, and, as ordinate, the whiteness of the obtained pulp, measured in index Elrepho. Each one of the charts has 3 curves *a*, *b* and *c* plotted for ozonized air rates and ozone titres given in the following table:

	Fig. 1	Fig. 2	Fig. 3
Ozonized air rate (l./hr.)	100	200	300
Ozone titre (in mg./l.):			
a	6.5	4.0	2.9
b	11.7	7.0	4.5
c	15.5	9.4	6.1

The bleaching method according to the present invention is limited neither by raw material nature nor by the process used for paper pulp fabrication. For example, pulps obtained from wood of resinous or long leaf trees and prepared by soda, sulfite or sulfate process fit quite well to the method according to the invention.

Pulp dryness degree is an important factor for the use of the method according to the present invention. Tests have shown the optimal value varies with regard to pulp nature, cooking and refining degrees. Our experiments have established the most favourable dryness rate is generally between 30 and 65%. For example, a beech kraft pulp, treated during 2 hours, at 20° C. with an ozonized air flow saturated with moisture, at a rate of 100 l./hr. and titrating 15.5 mg. ozone/liter has the following Elrepho whiteness values according to pulp concentration:

Dryness, percent	27	51	62	78
Elrepho whiteness	68	80	79.5	58

A eucalyptus kraft pulp, treated at a rate of 200 l./hr. with an ozone concentration of 9.5 mg./l. has the following values:

Dryness, percent	30	40	50	60
Elrepho whiteness	66	75	70	59

The pulp must preferably have a pH the nearest possible to neutrality, but a pH varying between 6 and 7.5 is not prejudicial to process application according to the present invention.

The most favourable reaction temperature is from 20 to 30° C. A comparative study has shown bleaching decreases when temperature increases. For example, a beech kraft pulp with 60% of dryness treated with an ozonized air stream of 100 l./hr., saturated with moisture and titrating 15.5 mg. O_3/l. gives the following Elrepho whiteness values, according to reaction temperature:

	Elrepho whiteness		
Treatment time	30 min.	1 hr.	2 hrs.
Temperature:			
25° C	58	78	87
45° C	50	71	85
65° C	36	50	71

The ozonized air stream saturated with moisture should be at the same temperature as that at which the pulp is maintained during reaction. Moreover, it must be taken care that the cellulosic material does not undergo notable temperature increase during ozonization. For this reason the equipment may possibly be provided with a cooling system.

Practically, the process according to the present invention offers a great ease in application since it consists of sending ozonized air to paper pulp in an only working stage. The treatment may be made in a discontinuous way, but also in a continuous one, which is interesting for industrial applications. Indeed experiment shows the method according to the invention may be made in a continuous way without residual ozone in the air at the bleaching tower outlet.

Though the process according to the invention may advantageously replace classical bleaching methods, it may alternatively be used in association with these classical methods. Thus, ozone treatment may be inserted into a bleaching sequence in several stages, ozonization being able to come before or to follow the usual treatments with hydrogen peroxide, hypochlorite or chlorine and soda.

The following examples, given in a non-limitative way, show how the process according to the invention may be applied.

EXAMPLE 1

A sample A of 25 g. of pine kraft unbleached pulp having a dryness rate of 40% (10 g. of dry extract) is shredded and put into a glass flask provided with an inlet tube and a gas recovery tube. The pulp has a pH of 7 and is maintained at a temperature of 20° C. An ozonized air stream titrating 15.5 mg./l. ozone is saturated with moisture at 20° C. in a moistener and enters the flask at a rate of 100 l./hr. The treatment is carried on for 2 hours.

A second identical sample, B, is treated in the same conditions but the ozonized air stream titrates 7.0 mg./l. ozone and is sent to the flask at a rate of 200 l./hr.

The main characteristics of the pulps obtained in this way are summarized in the following table:

	Non-treated sample	Sample A	Sample B
(1) Elrepho whiteness	22	77	74
Weight, g./m.^{2}	72.6	67.8	68.9
(2) Hand*	2.18	1.88	1.93
(3) Tensile length (m.)	3,250	4,050	4,200
(4) Bursting index	17	18	20

(1) AFNOR norm NF Q. 03. 008.
(2) AFNOR norm NF Q. 03. 016.
(3) AFNOR norm NF Q. 03. 004.
(4) AFNOR norm NF Q. 03. 014.
*The ratio thickness/weight in g./m.^{2}.

The values obtained for whiteness indexes are the more remarkable as starting paper pulp was especially difficult to bleach since it had a permanganate index of 39.

EXAMPLE 2

This example illustrates the very clear superiority of the bleaching with moistened ozonized air according to the present invention, with regard to the known process with dry ozonized air.

Two sample series of 50 g. of beech kraft unbleached pulp, of dryness 60% and a pH equal to 7, are treated according to the same working processes as in the Example 1, with an ozonized air flow titrating 15 mg./l. at a rate of 100 l./hr. at 25° C. For the first series the ozonized air is dry; for the second ones the ozonized air is saturated with moisture. The results are given in the following table:

	Dry ozonized air		Moistened ozonized air	
Treatment time	1 hr.	2 hrs.	1 hr.	2 hrs.
Elrepho whiteness	67	75	73	83
Shopper degree	14	15	14	14
Weight, g./m.^{2}	69.4	68.3	68.3	67.8
Hand*	2.05	2.05	2.14	2.05
Tensile length (m.)	2,550	2,450	2,700	2,750
Bursting index	8	7.5	11	10.5
(5) Tear index	51	41	48	42

(5) AFNOR norm NF Q. 03. 011.
*The ratio thickness/weight in g./m.^{2}.

The above tests make quiet clear the two aspects of the greater treatment efficiency with wet ozonized air with regard to bleaching with dry ozonized air:

on the one hand, for the same treatment time, whiteness is fairly improved (respectively 6 and 8 points for 1 and 2 hours of reaction);

on the other hand, for the same whiteness, obtained with wet ozonized air, after a treatment time much shorter than in the case of dry ozonized air, pulp characteristics are improved, especially with regard to breakdown length, bursting index and tear index.

It will be obvious to those skilled in the art that various changes may be made without departing from the spirit of the invention and therefore the invention is not limited to what is shown in the drawing and described in the specificaton.

What is claimed is:

1. In a method of bleaching a paper-making pulp by passing a gaseous stream containing ozone through the pulp, the improvement which consists in saturating the gaseous stream with moisture before passing it through the pulp, said pulp being an aqueous slurry having a dry consistency of 30 to 65%.

2. A method in accordance with claim **1** comprising: passing a gaseous mixture of ozone containing 2.5–18 mg. O_3/liter and having a moisture content near 100%,

to said pulp slurry having a pH of 6–7.5; maintaining the flow of said gaseous mixture for ½–2½ hours; and terminating said flow of gas.

3. A method in accordance with claim **1**, wherein said ozone is first generated in an atmosphere which is not saturated with water, and is then provided with said moisture content near 100%.

4. A method in accordance with claim **1**, wherein said ozone content is 4–16 mg. O_3/liter, said flow rate is 50–500 liters/hr., said treatment is carried out for 1–2 hours, said gaseous mixture has a moisture content of 100%, and aid pulp has a pH close to 7, and a temperature of 20–30° C.

5. A method in accordance with claim **1**, wherein said gaseous mixture consists essentially of air, water and ozone.

6. A method in accordance with claim **1**, wherein

said gaseous mixture consists essentially of oxygen, water and ozone.

7. A method in accordance with claim **1**, wherein the temperature of said gaseous mixture is maintained at approximately the same value as that of said pulp.

8. A method in accordance with claim **1** wherein the temperature of said pulp is about 20 to 30° C.

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HOWARD R. CAINE, *Primary Examiner.*

U.S. Cl. X.R.

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