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(54) **METHODE DE BLANCHIMENT D'UNE PATE A PAPIER A L'AIDE D'OZONE ET DE DIOXYDE DE CHLORE**

(54) **PROCESS FOR BLEACHING A PAPER PULP WITH OZONE AND CHLORINE DIOXIDE**

(57) Procédé de blanchiment d'une pâte à papier, dans lequel ladite pâte est soumise successivement à l'action de l'ozone, puis à celle du dioxyde de chlore, ou vice-versa. Selon l'invention, le procédé est caractérisé par le fait que la pâte à papier traitée est une pâte dite « à faible concentration », avec une consistance inférieure ou égale à environ 5 % en poids; le mélange de l'ozone avec la pâte s'effectue dans un agitateur rotatif, où la pâte est agitée à faible vitesse pendant que l'ozone est injecté dans la pâte; on obtient ainsi une pâte fluidisée, la vitesse tangentielle périphérique de la pâte sur les parois de l'agitateur rotatif étant inférieure ou égale à environ 12 m/s, mais supérieure ou égale à environ 2 m/s; le temps de contact entre l'ozone et la pâte se situe entre 1 et 20 min et la quantité d'ozone injectée dans l'agitateur rotatif varie de 1 à 20 kg d'ozone par t de pâte à papier à l'état sec; la pâte est maintenue à l'état fluidisé pendant presque toute la durée de la réaction avec l'ozone.

(57) Process for bleaching a paper pulp in which the said pulp is subjected successively to the action of ozone and then of chlorine dioxide, or vice versa. The process according to the invention is characterized in that the paper pulp treated is a so-called "low concentration" pulp with a consistency of less than or equal to approximately 5% by weight, the mixing of the ozone with the pulp being carried out in a rotary stirrer in which the pulp is stirred at a low speed while ozone is injected into the pulp, so as to obtain a fluidized pulp, the tangential peripheral speed of the pulp at the walls of the rotary stirrer being less than or equal to approximately 12 m/s but greater than or equal to approximately 2 m/s, the contact time between the ozone and the pulp being between 1 min and 20 min and the amount of ozone injected into the rotary stirrer being between 1 kg and 20 kg of ozone per t of paper pulp on a dry basis, the pulp being maintained in the fluidized state for substantially the entire duration of the reaction with the ozone.

ABSTRACT

Process for bleaching a paper pulp in which the said pulp is subjected successively to the action of ozone and then of chlorine dioxide, or vice versa. The process according to the invention is characterized in that the paper pulp treated is a so-called "low concentration" pulp with a consistency of less than or equal to approximately 5% by weight, the mixing of the ozone with the pulp being carried out in a rotary stirrer in which the pulp is stirred at a low speed while ozone is injected into the pulp, so as to obtain a fluidized pulp, the tangential peripheral speed of the pulp at the walls of the rotary stirrer being less than or equal to approximately 12 m/s but greater than or equal to approximately 2 m/s, the contact time between the ozone and the pulp being between 1 min and 20 min and the amount of ozone injected into the rotary stirrer being between 1 kg and 20 kg of ozone per t of paper pulp on a dry basis, the pulp being maintained in the fluidized state for substantially the entire duration of the reaction with the ozone.

PROCESS FOR BLEACHING A PAPER PULP WITH OZONE AND CHLORINE DIOXIDE

The present invention relates to a process for bleaching paper pulp in which the said pulp is subjected successively to the action of ozone and of chlorine dioxide, or vice versa.

In the past, chlorine was one of the bleaching agents which was most widely used for the bleaching of paper pulp, in particular for so-called chemical pulp. Chlorine dioxide or hypochlorite are also well known bleaching agents which make it possible both to remove the lignin in the cellulose and to improve the whiteness of the cellulose. As a general rule, the choice of the bleaching agent depends essentially on the type of paper which it is desired to produce from the treated pulp. When, for example, so-called kraft pulp is used to make very white writing paper, it is necessary to use a large amount of bleaching agent and to choose this agent from those having a faster and more selective action. Whatever the type of chlorinated bleaching agent used, organochlorine products are produced during the bleaching which generally have little solubility in the aqueous liquor for washing the pulp and large amounts of which are entrained or extracted from the pulp with the effluents at each stage of bleaching the pulp. A relatively low amount of these organochlorine products remains in the pulp itself. As a general rule, when chlorine is used and when it is desired to obtain very white products, it is necessary to use a much greater amount of chlorine compared with the processes in which the whiteness of the pulp obtained is less important.

As chlorinated effluent discharges have a particularly harmful effect on the environment, legislation has been passed in many countries so as to limit, if not completely ban, the use of chlorine and its derivatives in the bleaching of paper pulp, so as to limit the amount of organochlorine compounds in the aqueous wash liquors which it is subsequently necessary to treat. Lower limit values for the emission of organochlorine substances have thus been defined, amounts which are quantified by t of adsorbable organohalogen substances or AOX per tonne of pulp. For the moment, the maximum amounts per tonne of pulp are, depending on the country, limited to 1 or 2 t but, in a few years' time, it will be necessary to discharge effluents containing less than 0.5 t of AOX per tonne of pulp produced.

Some solutions have already been provided for reducing or removing organochlorine products in the process for bleaching paper pulp.

The simplest method consists in substituting non-chlorinated chemicals, such as oxygen, peroxides, such as hydrogen peroxide, ozone, peracetic acid, and the like, for the chlorinated chemicals used. Unfortunately however, none of these bleaching processes using non-chlorinated products has made it possible to obtain pulps for which the properties, such as the whiteness or the viscosity, have an acceptable value at a reasonable cost.

Another possibility for reducing the amount of organochlorine compounds is to reduce the amount of chlorine used, generally in the first bleaching stage. Various solutions have already been provided, such as increased delignification in the stage of cooking the pulp, as well as delignification with oxygen. These treatments, followed by an appropriate extraction stage, make it possible to reduce the content of lignin in the pulp, which is conveyed to the bleaching plant. However, these treatments do not make it possible to sufficiently reduce the concentration of organochlorine compounds in the bleached pulp and to bring the amount of residues to a sufficiently low value.

Another possibility consists in substituting chlorine dioxide for chlorine, which chlorine dioxide is a strong oxidizing agent compared with chlorine, making it possible to carry out a delignification comparable with that of chlorine, with a lower amount (less than half). This type of process is known in the literature under the abbreviation DE, preferably DEDED, the stage D being the stage of treatment with chlorine dioxide, the stage E being the conventional extraction stage.

For further details on these various treatments, reference may be made to the work by J.B. Casey, "Pulp and Paper, Chemistry and Chemical Technology", 3rd edition, Vol. 1, 1980, John Wiley & Son, New York, pages 694 to 696.

An experimental process for bleaching a paper pulp of "sulphite" type is also known from the journal "Pulp and Paper Science", March 1984, F. Granum, entitled "Influence of Bleaching Chemicals and Sequences on some Properties of Sulphite Pulp", pages J.25 or J.29, in which process numerous sequences are described, in particular sequences using oxygen or ozone, followed by sequences using chlorine dioxide.

A process for bleaching a kraft pulp intended for the manufacture of a paper is also known from EP 464,157, which process comprises a sequence of bleaching with pure or mixed chlorine dioxide, followed by a stage of bleaching with ozone, without an intermediate extraction stage, followed by an alkaline extraction as the third stage and finally ending with a fourth stage of bleaching with chlorine dioxide, this stage being the final stage of this bleaching process carried out in this order.

A process for bleaching a paper pulp according to a so-called DZ sequence, that is to say a first treatment with chlorine dioxide followed by a second treatment with ozone without an intermediate extraction stage between the two, is also known from Canadian Patent 2,031,850, in which process the two chemicals are injected at points separated from one another in the bleaching line. Such a process is supposed to decrease the production of AOX. However, all the examples given were carried out on pulp delignified beforehand with oxygen.

Canadian Patent 2,031,848 also discloses a process similar to that disclosed above in Canadian Patent 2,031,850 but in any order, that is to say in fact describing ZD or DZ sequences. Here again, a preliminary stage of delignification with oxygen is necessary, as is disclosed in all the examples.

In these two Canadian patents and in the abovementioned European patent, all the implementational examples are exclusively based on a paper pulp of medium consistency.

It is generally expected by a person skilled in the art that the higher the consistency of the pulp, the better the efficiency should be of the treatment with chemicals of the D and Z type, provided that the mixing is carried out in a mixer with a very high speed. This is why, until now, none of these processes has been developed with so-called low consistency pulp, that is to say comprising a much greater amount of water than a medium or high consistency pulp.

However, paper pulp plants operating with low consistency pulp currently face a number of problems. A number of plants currently operate with CD sequences, that is to say a first stage of bleaching with chlorine, followed by a second stage of bleaching with chlorine dioxide (intermediate solution already mentioned above), which process, as was indicated above, is not satisfactory with respect to standards which will soon come into force relating to discharges of AOX. In these plants, which currently operate with low consistency pulps, all the equipment used is specific to low consistency pulp, in particular the mixers, the dimensions of the pipework and of the intermediate storage devices, and, generally, all the manufacturing equipment. With the processes currently known for preventing an excessively high concentration of AOX products in the discharges, it is thus necessary, for the conversion of these plants, to equip them with medium or high consistency equipment, so as to meet the standards. This means that it is necessary to replace all the existing equipment by new equipment in these plants, which means an investment of millions of dollars.

There currently therefore does not exist a process which generates a low amount of AOX, that is to say less than 0.5 t of AOX per tonne of paper pulp, and which uses a treatment of the pulp at low consistency, that is to say a pulp with a consistency ≤ 5%.

It is an object of the present invention to provide a solution to the problem thus posed.

The process according to the invention is characterized in that the paper pulp treated is a so-called "low concentration" pulp with a consistency of less than or equal to approximately 5% by weight, the mixing of the ozone with the pulp being carried out in a rotary stirrer in which the pulp is stirred at a low speed while ozone is injected into the pulp, so as to obtain a fluidized pulp, the tangential peripheral speed of the pulp at the walls of the rotary stirrer being less than or equal to approximately 12 m/s but greater than or equal to approximately 2 m/s, the contact time between the ozone and the pulp being between 1 min and 20 min and the amount of ozone injected into the rotary stirrer being between 1 kg and 20 kg of ozone per t of paper pulp on a dry basis, the pulp being maintained in the fluidized state for substantially the entire duration of the reaction with the ozone.

The ozone is preferably injected as a mixture with oxygen, preferably in the proportion of 3 to 20% by volume of ozone in the oxygen, the oxygen also being in contact with the pulp for substantially the same duration as the ozone and producing a complementary and simultaneous delignification and/or bleaching action on the pulp.

At the end of the stirring stage, the oxygen is recovered, filtered to retain the undesirable impurities and optionally recycled to the inlet of the ozonizer.

Use will preferably be made of an ozonizer in which oxygen is introduced at a pressure greater than atmospheric pressure, so as, on the one hand, to optimize the yield from the ozonizer and, on the other hand, on account of the pressure drops in the latter, to obtain a mixture of oxygen and of ozone at a pressure greater than atmospheric pressure (preferably between 1.3 bar and 2.5 bar, absolute pressure) but less than 15 bar absolute, generally between 1 and 3 bar absolute. The gaseous mixture can thus be introduced directly into the pulp, without having to be compressed before being injected.

The tangential peripheral speed of the pulp will preferably be less than 9 m/s and more preferably less than 6 m/s, which, in the case of a cylindrical stirrer with a diameter of approximately 1 metre, represents a rotational speed of less than approximately 120 revolutions per minute.

The amount of ozone per t of dry pulp is preferably between 2 and 10 kg, while the duration of treatment with ozone in the stirred reactor is preferably between 2 and 10 min. As regards the chlorine dioxide, the amounts vary between 1 and 20 kg per t of dry pulp, preferably from 2 to 10 kg per t of dry pulp.

By using the process according to the invention, effluents having an amount of AOX of 0.1 to 0.2 kg per tonne of dry pulp produced are thus easily obtained. The plant designed or used for a CD or DC sequence is not changed, the plant for injection of chlorine simply being replaced by a plant for injection of ozone, in the amounts mentioned above. Another considerable advantage of the invention is that the mechanical properties of the pulp are retained or even improved.

Rotary stirrer or stirred reactor is understood to mean a stirrer, preferably cylindrical, comprising one or more paddles which are capable of causing the entire liquid (low consistency pulp) to rotate with a tangential speed, measured at the periphery of a section of the cylinder, defined above as being the tangential peripheral speed of the pulp.

The general characteristics of the stirred reactors are described in the article entitled "The mixing-rate number for agitator stirred-tank", Chemical Engineering, October 11, 1976, pages 141 to 143.

Another advantage of the invention is that it is not necessary to use an intermediate receptacle or flash tank (for example, see Canadian Patent 2,031,848), into which receptacle, after mixing the pulp and the reactants in the mixer, the pulp is poured in order to continue the reaction between the pulp and the ozone, so as to improve the bleaching of the pulp. In the brochure from the company Kvaerner Pulping Technologies AB entitled "Kvaerner MC® Mixer", second page, it is explained that correct fluidization of a pulp with a mixer especially designed for paper pulp can only be achieved with pulps having a consistency of the order of or greater than 10% (so as to achieve a rheological behaviour of the pulp substantially identical to that of water). For this, the rotational speed must be greater than approximately 1800 revolutions per minute, i.e. a tangential peripheral speed of approximately 30 m/s for a diameter of approximately 30 cm for an industrial mixer. The contact between the pulp and the ozone in the mixer lasts at most 10 seconds. Furthermore, in the process according to the invention, it is not necessary to provide a stage of delignification with oxygen prior to the DZ sequence according to the invention.

The stage of treatment with ozone will take place before or after treatment with chlorine dioxide.

Of course, the process of the invention applies to the case where ozone alone is injected, without injection of chlorine dioxide, or, if the stage of injection of ozone is preceded or followed by any type of bleaching stage or sequence with any well known bleaching agent mentioned above, including another stage with ozone similar to or different from that according to the present invention.

Furthermore, throughout this description, it has been assumed that the rotational speed of the paddles of the stirrer is comparable to the rotational speed of the pulp, in particular at the walls (tangential peripheral speed). In practice, differences due to local turbulences in the pulp may be found.

Example 1

In this example , a sample of non oxygen delignified softwood kraft pulp - Kappa 27 - is treated according the invention at low consistency in ~~a specially designed~~ mixer. Pulp is first delignified with chlorine dioxide by adding 2 % ClO_2. Then the sample is divided in two portions; the first one -sample A- , after washing , is treated in a Ep stage according the following conditions :

NaOH charge : 1.5 %
H_2O_2 charge : 0.25 %
Temperature : 75° C
Time : 120 minutes
Consistency : 10 %

The second portion -sample B- ,before any washing, is directly treated with O_3 under the following operating conditions :

Temperature : 50°C
Pressure : atmospheric
Pulp consistency : 2.5 %
O_3 concentration in O_2 : 10 % by weight
Mixing time : 6 minutes
Peripherical mixer rotating speed : 4.1 m/s
O_3 injected : 5 kg/t or 0.5 % on pulp
O_3 consumption efficiency : 95 %

After reaction sample B is submitted to the same washing and then Ep stage as with sample A. Sample B exhibits after D Ep treatment a Kappa of 3.4 compared to 5.6 for sample A after DZ Ep reflecting the efficiency of the O3 treatment carried out in such conditions.

Example 2

In this example , an O2 delignified kraft eucalyptus pulp - Kappa 9.0 , Brightness 45.8 % ISO- is used for comparing O3 treatments in a DZ sequence with conventional high shear mixing at medium consistency (sample A) and low shear mixing at low consistency (sample B). For reference , a first pulp is treated according the D Eo D sequence. Operating conditions for the reference are :

D stage

Temperature : 55°C
Residence time : 45 minutes
ClO2 charge : 1.3 % (as pure ClO2)
Consistency : 11 %

Eo stage

Temperature : 70°C
Residence time : 125 minutes
NaOH charge : 1.3 %
Consistency : 12 %
O2 pressure : 2 bars

Final D stage

Temperature : 70°C
Residence time : 90 minutes
ClO2 charge : 0.6 % (as pure ClO2)
Consistency : 11 %

Results obtained on this reference sample are :

Kappa after D Eo : 0.9

Brightness after D Eo : 73.8 % ISO

Brightness after D Eo D : 88.1 % ISO

DZ Eo D sequences

In both cases, ClO2 and O3 are added sequentially, O3 being added after complete consumption of ClO2 in the first step, before any washing.

For sample A, D stage conditions are identical to the reference except the ClO2 charge which is reduced to 0.48%. Then 0.4 % (or 4 kg/t on pulp) O3 is added under high shear mixing conditions which are :

O3 pressure : 9 bars

O3 concentration in O2 : 9.5 % by weight

Pulp consistency : 11 %

Temperature : 55°C

Peripherical mixer rotating speed : 78 m/s

Next stages are carried out according conditions identical to the reference except the ClO2 charge in the final D stage which is reduced to 0.4 %. Results obtained are :

Kappa after DZ Eo : 0.9

Brightness after DZ Eo : 79.2 % ISO

Brightness after DZ EoD : 88.5 % ISO

Sample B is treated at low consistency both with ClO2 and O3 ; other D stage conditions are identical to the reference except the ClO2 charge which is reduced to 0.45 % and pulp consistency which is reduced to 2.5 %. Then 0.4 % (or 4 kg/t on pulp) O3 is added under low shear mixing conditions which are :

O3 pressure : 2 bars

O3 concentration in O2 : 9.5 % by weight

Pulp consistency : 2.5 %

Temperature : 55°C

Peripherical mixer rotating speed : 11 m/s

Next stages are carried out according conditions identical to the reference except the ClO2 charge in the final D stage which is reduced to 0.4 % . Results obtained are :

Kappa after DZ Eo : 0.9

Brightness after DZ Eo : 79.0 % ISO

Brightness after DZ EoD : 88.3 % ISO

These examples show clearly that the O3 treatment can be combined with a ClO2 stage in a DZ sequence while carried out at low consistency under appropriate fluidised conditions with at least the same efficiency as when performed at medium consistency. This is reflected among other things by the savings in ClO2 when comparing the various charges in ClO2 used to reach 88 % ISO brightness. For the reference 1.9 % ClO2 is needed while for the DZ Eo D only 0.88 % and 0.85 % are required for respectively medium and low consistency treatments

CLAIMS

1. Process for bleaching a paper pulp in which the said pulp is subjected successively to the action of ozone and then of chlorine dioxide, or vice versa, which process is characterized in that the paper pulp treated is a so-called "low concentration" pulp with a consistency of less than or equal to approximately 5% by weight, the mixing of the ozone with the pulp being carried out in a rotary stirrer in which the pulp is stirred at a low speed while ozone is injected into the pulp so as to obtain a fluidized pulp, the tangential peripheral speed of the pulp at the walls of the rotary stirrer being less than or equal to approximately 12 m/s but greater than or equal to approximately 2 m/s, the contact time between the ozone and the pulp being between 1 min and 20 min and the amount of ozone injected into the rotary stirrer being between 1 kg and 20 kg of ozone per t of paper pulp on a dry basis, the pulp being maintained in the fluidized state for substantially the entire duration of the reaction with the ozone.

2. Process for bleaching a paper pulp according to Claim 1, characterized in that the ozone is injected as a mixture with oxygen, preferably in the proportion of 3 to 20% by volume of ozone in the oxygen, the oxygen also being in contact with the pulp for substantially the same duration as the ozone and producing a complementary and simultaneous delignification and/or bleaching action on the pulp.

3. Process for bleaching a paper pulp according to Claim 2, characterized in that the oxygen is recovered in order to be optionally recycled.

4. Process for bleaching a paper pulp according to one of Claims 1 to 3, characterized in that the pressure of the ozone and of the oxygen introduced into the pulp is between 1 and 15 bar absolute.

5. Process for bleaching a paper pulp according to Claim 4, characterized in that the pressure of the

ozone and of the oxygen introduced into the pulp is between 1 and 3 bar, preferably 1.3 and 2.5 bar, absolute.

6. Process for bleaching a paper pulp according to one of Claims 1 to 5, characterized in that the tangential peripheral speed is less than or equal to 9 m/s, preferably 6 m/s.

7. Process for bleaching a paper pulp according to one of Claims 1 to 6, characterized in that the amount of ozone per t of dry pulp is between 2 and 10 kg.

8. Process for bleaching a paper pulp according to one of Claims 1 to 7, characterized in that the amount of chlorine dioxide introduced into the pulp is between 1 and 20 kg per t of dry pulp, preferably from 2 to 10 kg per t of dry pulp.