(54) Titre: PROCEDE DE BLANCHIMENT AU DIOXYDE DE CHLORDE DE PATES CHIMIQUES UTILISANT DE L'HYDROXYDE DE MAGNESIUM OU DE L'OXYDE DE MAGNESIUM

(54) Title: PROCESS OF CHLORINE DIOXIDE BLEACHING OF CHEMICAL PULPS USING MAGNESIUM HYDROXIDE OR MAGNESIUM OXIDE

(57) Abrégé/Abstract:
The present invention provides an improved process for chlorine dioxide bleaching of chemical pulps in an aqueous suspension, which uses magnesium hydroxide or magnesium oxide. The process involves the addition of magnesium hydroxide or magnesium oxide to the pulp, in addition to chlorine dioxide, maintaining the mixture at a pH between about 2.5 to 7.5 for about 1 or more hours, most suitably between about 1 - 4 hours. This process can be used in the D1 or D2 stage of a typical D0EopD1E2D2 bleaching sequence, as well as in the chlorine dioxide brightening stage of other three, four, five, and six-stage bleaching sequences of either the so-called ECF process, or those containing elemental chlorine (Cl2). The temperature is between about 40 to about 90°C, and the pulp consistency is between about 1 to about 16%.
PROCESS OF CHLORINE DIOXIDE BLEACHING OF CHEMICAL PULPS USING MAGNESIUM HYDROXIDE OR MAGNESIUM OXIDE

FIGURE 2

The present invention provides an improved process for chlorine dioxide bleaching of chemical pulps in an aqueous suspension, which uses magnesium hydroxide or magnesium oxide. The process involves the addition of magnesium hydroxide or magnesium oxide to the pulp, in addition to chlorine dioxide, maintaining the mixture at a pH between about 2.5 to 7.5 for about 1 or more hours, most suitably between about 1 - 4 hours. This process can be used in the D1 or D2 stage of a typical D_1, D_2, D_3, D_4 bleaching sequence, as well as in the chlorine dioxide brightening stage of other three, four, five, and six-stage bleaching sequences of either the so-called ECF process, or those containing elemental chlorine (Cl_2). The temperature is between about 40 to about 90°C, and the pulp consistency is between about 1 to about 16%.
PROCESS OF CHLORINE DIOXIDE BLEACHING OF CHEMICAL PULPS USING MAGNESIUM HYDROXIDE OR MAGNESIUM OXIDE

FIELD OF INVENTION

The present invention is related to the bleaching of chemical pulps, in particular, to an improved process which uses chlorine dioxide as the primary chemical.

BACKGROUND OF THE INVENTION

Chlorine dioxide is the main chemical in the bleach plant for the production of bleached chemical pulps. Such a bleaching process is normally carried out in multiple processing stages, utilizing chlorine dioxide, caustic soda, oxygen, and hydrogen peroxide. A typical process is a $D_0E_{op}D_1E_2D_2$ sequence, where:

$D_0$: chlorine dioxide delignification, in many cases some acids, such as sulphuric acid, or spent acid from the chlorine dioxide generator, is used to control the pH of 2-3;

$E_{op}$: alkaline extraction with caustic soda, a small amount of oxygen and hydrogen peroxide can be added, and the end pH is in the range of 10-11.5;

$D_1$: first chlorine dioxide brightening stage; sodium hydroxide is usually added to control the end pH of 3-6;

$E_2$: the second alkaline extraction; a small amount of hydrogen peroxide may be added, the end pH is in the range of 9.5-11.5;

$D_2$: the second chlorine dioxide brightening stage, a small amount of sodium hydroxide is usually added to control the end pH of 3.5-7.0.
Chlorine dioxide is one of the most expensive chemicals used in the bleaching of chemical pulps. Improving its efficiency is desirable to decrease the overall bleaching cost.

U.S. Pub. No. 20070079944 to Amidon et al. discloses an omnibus process of pulping and bleaching lignocellulosic materials. With regard to the bleaching process, Amidon et al. teaches contacting the pulped product with chlorine dioxide in the presence of O₂. The O₂ addition, however, has an inherent problem due to the lower viscosity, and Amidon et al. addressed this problem by adding magnesium hydroxide. It is suggested in Amidon et al. that the addition of Mg(OH)₂ exploits Mg cation's property of disrupting the free radical propagation mechanism by forming complexes with superoxide anions. Although Amidon et al. reported improved viscosity and increased brightness through the oxygen/chlorine dioxide/magnesium hydroxide bleaching process, there still remains certain downsides of adding O₂. For example, although oxygen itself is cheaper than chlorine dioxide, the set-up to add the oxygen into the bleaching process is expensive.

Therefore, there is a need to provide a method of bleaching chemical pulps, in particular, to a more economical process which uses chlorine dioxide as the primary chemical.

SUMMARY OF THE INVENTION

It has been discovered that magnesium hydroxide (or magnesium oxide) can be effectively added to the chlorine dioxide bleaching, resulting in unexpected improvements in the bleaching process. At the same chlorine
dioxide charge, a higher brightness can be achieved and the production cost can be decreased making the process more economical.

The present invention provides an improved process for chlorine dioxide bleaching of chemical pulps in an aqueous suspension, which uses magnesium hydroxide or magnesium oxide. The novelty comprises the addition of magnesium hydroxide (or magnesium oxide) to pulp, in addition to chlorine dioxide, maintaining the mixture at a pH between about 2.5 - 7.5 for about 1 or more hours, most suitably between about 1 - 4 hours. This novel process can be used in the D₁ or D₂ stage of a typical D₀E₀D₁E₂D₂ bleaching sequence, as well as in the chlorine dioxide brightening stage of other three, four, five, and six-stage bleaching sequences of either the so-called ECF process, or those containing elemental chlorine (Cl₂). The temperature is between about 50-85°C, and the pulp consistency is maintained in a range between about 1 to about 16% weight percentage on dried mass of pulp, and preferably between about 3-12%.

Thus, an embodiment of the present invention provides a process for bleaching chemical pulp of the type characterized by a D₀E₀D₁E₂D₂ bleaching sequence in which

D₀: chlorine dioxide delignification, with the pH controlled in a range from about 2 to about 3;

E₀: alkaline extraction with caustic soda, pH is in the range of 10-11.5;

D₁: first chlorine dioxide brightening stage with pH controlled in a range from about 3 to about 6;

E₂: the second alkaline extraction, the end pH is in the range from about 9.5 to about 11.5;
D₂: the second chlorine dioxide brightening stage, the end pH controlled in a range from about 3.5 to about 7.0, wherein the process comprises the steps of:

bleaching chemical pulps in the D₁ and/or D₂ stages using chlorine dioxide, including adding chlorine dioxide and magnesium hydroxide or magnesium oxide in the absence of oxygen to a suspension of the chemical pulp to form a mixture, wherein the chlorine dioxide and magnesium hydroxide are added in a sequential order or simultaneously, including maintaining the mixture at a pH between about 2.5 to about 7.5 for about 1 or more hours, and maintaining the mixture at a temperature in a range from about 40°C to about 90°C, and maintaining a pulp consistency in a range between about 1 to about 16% weight percentage on dried mass of pulp.

The method disclosed herein provides more efficient chlorine dioxide bleaching in the chemical pulp bleaching process which decreases the production cost of the chemical pulp bleaching process while at the same time provides a higher pulp brightness with a given chlorine dioxide charge.

A further understanding of the functional and advantageous aspects of the invention can be realized by reference to the following detailed descriptions and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood from the following detailed descriptions thereof taken in connection with the accompanying drawings, which form a part of this application, and in which:
Figure 1 is a process flow sheet of a conventional chlorine dioxide bleaching process; and

Figure 2 shows the process flow sheet of a chlorine dioxide bleaching process using magnesium hydroxide (magnesium oxide) in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Generally speaking, the systems described herein are directed to the bleaching of chemical pulps, in particular, to an improved process which uses chlorine dioxide as the primary chemical. As required, embodiments of the present invention are disclosed herein. However, the disclosed embodiments are merely exemplary, and it should be understood that the invention may be embodied in many various and alternative forms. The Figures are not to scale and some features may be exaggerated or minimized to show details of particular elements while related elements may have been eliminated to prevent obscuring novel aspects. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention. For purposes of teaching and not limitation, the illustrated embodiments are directed to a bleaching process for bleaching chemical pulp which uses chlorine dioxide as the primary chemical.

As used herein, the term "about", when used in conjunction with ranges of dimensions of particles or other physical properties or characteristics, is meant to cover slight variations that may exist in the upper and lower limits of
the ranges of dimensions so as not to exclude embodiments where on average most of the dimensions are satisfied but where statistically dimensions may exist outside this region. It is not the intention to exclude embodiments such as these from the present invention.

As discussed in the Background above, chlorine dioxide is the main chemical in the bleach plant for the production of bleached chemical pulps. The bleaching process is normally carried out in multiple processing stages, utilizing chlorine dioxide, caustic soda, oxygen, and hydrogen peroxide. The typical process uses a $D_0E_{op}D_1E_2D_2$ sequence, where:

1. $D_0$: chlorine dioxide delignification, with the pH controlled in a range from about 2 to about 3;
2. $E_{op}$: alkaline extraction with caustic soda, pH is in the range of 10-11.5;
3. $D_1$: first chlorine dioxide brightening stage with pH controlled in a range from about 3 to about 6;
4. $E_2$: the second alkaline extraction, the end pH is in the range from about 9.5 to about 11.5;
5. $D_2$: the second chlorine dioxide brightening stage, the end pH controlled in a range from about 3.5 to about 7.0.

**Figure 1** shows the process flow sheet of the conventional chlorine dioxide bleaching process; the pulp from the previous stage is added with chlorine dioxide and sodium hydroxide via a mixer, and then pumped via a pump to either a up-flow or down-flow bleaching tower; after exiting from the bleaching tower, the bleached pulp is washed in a washer, chlorine dioxide and/or sodium hydroxide may also be mixed to the pulp via the pump so that the pump functions for mixing and pumping.
Figure 2 shows the process concept of the chlorine dioxide bleaching using magnesium hydroxide (magnesium oxide); the pulp form the previous stage is added with chlorine dioxide and magnesium hydroxide via a mixer, and then pumped via a pump to either an up-flow or down-flow bleaching tower; after exiting from the bleaching tower, the bleached pulp is washed in a washer, chlorine dioxide and/or magnesium hydroxide/magnesium oxide may also be mixed to the pulp via the pump so that the pump functions for mixing and pumping. If desirable, sodium hydroxide can be added to the process. This process is carried out in the absence of pumping in oxygen.

A small amount of magnesium hydroxide (magnesium oxide) can also be used in the $E_{op}$ and $E_2$ stages of the $D_0E_{op}D_1E_2D_2$ sequence, to partially substitute for sodium hydroxide.

The pulp consistency is maintained in a range between about 1 to about 16% weight percentage on dried mass of pulp, and preferably between about 3-12%.

Without being limited by any theory, it is believed that the unexpected improvement of the chlorine dioxide bleaching by using magnesium hydroxide is due to the following reasons. First, the pH in the process is more stable and less variable, secondly, the charged chlorine dioxide in the process is used more effectively, and thirdly, magnesium cation has a positive effect on the bleaching performance.

EXAMPLE
A softwood kraft pulp, which is treated in a \( D_0E_0 \) sequence and has a Kappa \# of 5.1 and pulp brightness of 49.3%, was subjected to a conventional chlorine dioxide bleaching under the conditions of:

\[
\text{ClO}_2 \text{ charge: } 1.72\% \\
\text{NaOH charge: } 0.60 \%
\]

69°C, 265 min, 11% pulp consistency

The resulting pulp has a pulp brightness of 79.9% ISO.

The same \( D_0E_0 \) treated pulp, with a Kappa \# of 5.1 and pulp brightness of 49.3%, was subjected to the novel chlorine dioxide bleaching by using magnesium hydroxide under the conditions of:

\[
\text{ClO}_2 \text{ charge: } 1.72\% \\
\text{Magnesium hydroxide: } 0.44\%
\]

69°C, 265 min, 11% pulp consistency

The resulting pulp has a pulp brightness of 84.7%, 4.8 units higher than the control, which clearly demonstrates the superior performance of the novel chlorine dioxide bleaching by using magnesium hydroxide.

Thus, broadly speaking, the present invention provides a process for chlorine dioxide bleaching of chemical pulps, such as the \( D_1 \) and/or \( D_2 \) stage of a typical \( D_0E_0D_1E_2D_2 \) sequence, comprising the steps of mixing pulp slurry with magnesium hydroxide and chlorine dioxide, maintaining the mixture at a pH between about 2.5 - 7.5 for about 1 or more hours in a temperature of about 40 - 90°C. The required amount of magnesium hydroxide and chlorine dioxide can be added either sequentially or simultaneously.

As used herein, the terms "comprises", "comprising", "including" and "includes" are to be construed as being inclusive and open ended, and not
exclusive. Specifically, when used in this specification including claims, the terms "comprises", "comprising", "including" and "includes" and variations thereof mean the specified features, steps or components are included. These terms are not to be interpreted to exclude the presence of other features, steps or components.

The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.
1. A process for bleaching chemical pulp of the type characterized by a $D_0E_{op}D_1E_2D_2$ bleaching sequence in which

$D_0$: chlorine dioxide delignification, with the pH controlled in a range from about 2 to about 3;

$E_{op}$: alkaline extraction with caustic soda, pH is in the range of 10-11.5;

$D_1$: first chlorine dioxide brightening stage with pH controlled in a range from about 2.5 to about 7.5;

$E_2$: the second alkaline extraction, the end pH is in the range from about 9.5 to about 11.5;

$D_2$: the second chlorine dioxide brightening stage, the end pH controlled in a range from about 2.5 to about 7.5, wherein the process comprises the steps of:

bleaching chemical pulps in the $D_1$ and/or $D_2$ stages using chlorine dioxide, including adding chlorine dioxide and magnesium hydroxide or magnesium oxide in the absence of oxygen to a suspension of the chemical pulp to form a mixture, wherein the chlorine dioxide and magnesium hydroxide are added in a sequential order or simultaneously, including maintaining the mixture at a pH between about 2.5 to about 7.5 for about 1 or more hours, and maintaining the mixture at a temperature in a range from about 40°C to about 90°C, and maintaining a pulp consistency in a range between about 1 to about 16% weight percentage on dried mass of pulp.
2. The process according to claim 1 wherein said temperature is maintained in a range from about 55°C to about 80°C.

3. The process according to claim 1 or 2 including maintaining the mixture at a pH between about 3 to about 7 for between about 1 to about 4 hours.

4. The process according to claim 1 or 2 wherein said pH of the mixture is maintained in a range from about 3 to about 6.

5. The process according to claim 1, 2, 3 or 4 wherein said pulp consistency is maintained between about 3 to about 12%.