The invention is directed to a method for reducing fluorescence in recycled pulp, wherein the method includes: contacting a pulp slurry containing fluorescent agents with chlorine dioxide; and contacting the pulp slurry with a sodium hypochlorite component, in an amount sufficient to reduce the fluorescence of the pulp; wherein the pulp is contacted with sodium hypochlorite component simultaneous with or after contact with chlorine dioxide.
Title: PROCESS FOR REDUCING FLUORESCENCE IN PULP

Abstract: The invention is directed to a method for reducing fluorescence in recycled pulp, wherein the method includes: contacting a pulp slurry containing fluorescent agents with chlorine dioxide; and contacting the pulp slurry with a sodium hypochlorite component, in an amount sufficient to reduce the fluorescence of the pulp; wherein the pulp is contacted with sodium hypochlorite component simultaneously with or after contact with chlorine dioxide.
PROCESS FOR REDUCING FLUORESCENCE IN PULP

FIELD OF THE INVENTION

The field of the invention relates to production of pulp and paper from pulp sources containing fluorescent agents, such as recycled paper. More particularly, it refers to decreasing or eliminating fluorescence in pulp and paper.

BACKGROUND OF THE INVENTION

Fluorescence is an optical phenomenon, whereby light is absorbed at non-visible wavelengths (e.g., ultraviolet), and then re-emitted at visible wavelengths. Chemicals referred to as “fluorescent whitening agents” or “optical brightening agents,” or “FWA’s” or “OBA’s,” are often added to the furnish in the production of many fine papers, e.g., printing or copying paper, as well as tissue and towel grade products, to enhance the apparent brightness of the product. FWA’s are typically stilbene-based compounds and their chemical derivatives.

When paper products containing FWA’s are recycled the majority of the fluorescent compounds stay with the fiber through the recycling process. This has been reported to cause some operational problems due to color and brightness control in de-inked pulp Mills, and in paper Mills using recycled fiber. FWA’s can modify the apparent color of de-inked pulps, as well as impair or change the final quality of the finished product. The presence of FWA’s can affect the response of UV-based on-line color sensors and can negatively affect the performance of control loops.

In addition, it has been suspected that FWA’s can pose a potential health hazard, by leaching out of paper products made with recycled fibers. FWA’s are not permitted in some food-grade packaging. Therefore, FWA’s would need to be removed from recycled fibers intended for such food-grade applications.

Accordingly, there exists a need to reduce or remove FWA’s from recycled pulp in an efficient manner.
SUMMARY OF THE INVENTION

It has been found that fluorescence in a recycled pulp can be reduced by a process that involves contacting the pulp, which contains fluorescent agents, with a combination of chlorine dioxide (ClO₂) and sodium hypochlorite (or a derivative of sodium hypochlorite) in amounts sufficient to reduce the fluorescence of the pulp, wherein the pulp is contacted with the sodium hypochlorite simultaneous with or after the pulp is contacted with ClO₂.

In one embodiment, ClO₂ and a sodium hypochlorite component are added to the pulp simultaneously or the sodium hypochlorite component is added a short time after the addition of the ClO₂, wherein the sodium hypochlorite component contains sodium hypochlorite, a derivative of sodium hypochlorite, or mixtures thereof.

In one embodiment, ClO₂ and sodium hypochlorite are added to the pulp simultaneously or the sodium hypochlorite is added a short time after the addition of the ClO₂. In embodiments of the invention, sodium hypochlorite is added less than about 2 minutes, or less than about 1 minute, or less than about 30 seconds, or less about 10 seconds, or less than about 5 seconds, or less than about 1 second, after the addition of the ClO₂. In one embodiment, ClO₂ and sodium hypochlorite are added to the pulp simultaneously.

In embodiments of the invention, the amount of ClO₂ added to the pulp is in the range from about 4 to about 15 kg/t (1000 kg) of dry pulp, or about 5 to about 10 kg/t, or about 6 to about 8 kg/t. In embodiments of the invention, the amount of sodium hypochlorite added to the pulp is in the range of about 2 to about 12.5 kg/t of dry pulp, or about 2.5 to about 8 kg/t, or about 3 to about 6 kg/t. In one embodiment, ClO₂ is added in an amount greater than the amount of sodium hypochlorite (on a weight basis). In embodiments of the invention, the weight ratio of ClO₂ to sodium hypochlorite is in the range from 1:1 to 3:1, or 1.1:1 to 2:1, or 1.2:1 to 1.8:1, or about 3:2. In other embodiments of the invention, lower chemical charges are also contemplated and even if fluorescence is not reduced to zero or near zero, a smaller amount of reduction in fluorescence is also contemplated to be within embodiments of the invention.
Additional objects, advantages and novel features will be apparent to those skilled in the art upon examination of the description that follows.

**BRIEF DESCRIPTIONS OF THE DRAWINGS**

FIGURE 1 is a schematic of fluorescence reduction process using an up flow reaction vessel.

FIGURE 2 is a graph showing the effect of the delay in hypochlorite addition on brightness and fluorescence for Example 1.

FIGURE 3 is a graph showing the effect of the delay in hypochlorite addition on L-value for Example 1.

FIGURE 4 is a graph showing the effect of the delay in hypochlorite addition on whiteness and tint for Example 1.

FIGURE 5 is a graph showing the effect of the delay in hypochlorite addition on a and b values for Example 1.

FIGURE 6 is a graph showing the effect of chemical sequence on fluorescence for Example 2.

FIGURE 7 is a graph showing the effect of chlorine dioxide charge on fluorescence for Example 3.

FIGURE 8 is a graph showing the effect of chlorine dioxide charge on pH and residual chlorine dioxide for Example 3.

FIGURE 9 is a graph showing the effect of chlorine dioxide charge on pH and residual chlorine dioxide for Example 3.

FIGURE 10 is a graph showing the effect of delay in sodium hypochlorite addition on brightness and fluorescence for Example 4.

FIGURE 11 is a graph showing the effect of delay in sodium hypochlorite addition on whiteness and tint for Example 4.

**DETAILED DESCRIPTION OF THE INVENTION**

In one aspect, the process according to the invention involves processing waste paper to form a pulp slurry that includes pulp and fluorescent agents, e.g., FWA’s, and applying chlorine dioxide either prior to or simultaneously with sodium
hypochlorite to a process stream containing fluorescence (pulp, paper). The pulp
slurry can have a consistency in the range of about 4% to about 20%, or about 6% to
about 18%, or about 8% to about 16% prior to adding the chlorine dioxide. It is
possible to operate at a consistency lower than 4%, e.g., to match an existing
process stream in a pulp or paper mill, and still receive a benefit from the present
invention, however it is believed that somewhere below 1% the benefits of adding
sodium hypochlorite are lost. In an embodiment, the delay between the two chemical
additions is not so long that residual chlorine dioxide is no longer present.
 Preferably, there should be at least five minutes of reaction time remaining after
sodium hypochlorite addition.

In embodiments of the invention, the process is described as contacting the pulp with
chlorine dioxide and sodium hypochlorite. By “contacting” is meant that the chemical
(contacting the pulp) is added to the pulp slurry or is formed in situ by the reaction of
precursor chemicals that form the desired chemical. For example, chlorine dioxide or
sodium hypochlorite can be formed in situ in the pulp slurry and the other chemical
can be added to the slurry in accordance with the invention, or both the chlorine
dioxide and sodium hypochlorite can be formed in situ. In embodiments of the
invention, chlorine dioxide or sodium hypochlorite, or both, can be formed in situ in
separate process equipment or process streams and then added to the pulp slurry.

Although embodiments of the invention are described herein with respect to
contacting (the pulp) with or adding sodium hypochlorite (to the pulp), it should be
understood that other embodiments of the invention contemplate using a sodium
hypochlorite derivative instead of (or in combination with) the sodium hypochlorite.
By “sodium hypochlorite derivative” is meant one or more chemical compounds that
are produced as a result of introducing sodium hypochlorite into the pulp slurry along
with chlorine dioxide in accordance with the present invention, by dissociation of
sodium hypochlorite or by reaction of sodium hypochlorite with other compounds in
the slurry during the fluorescence reduction process, the presence of which improves
fluorescence reduction compared to chlorine dioxide alone. For example, it is
believed that under certain conditions sodium hypochlorite will form hypochlorous
acid in solution in the pulp slurry. Accordingly, hypochlorous acid is considered a
derivative of sodium hypochlorite and addition of hypochlorous acid alone, or in
combination with sodium hypochlorite, to the pulp and chlorine dioxide is contemplated to be within the scope of an embodiment of the present invention.

An example of a process flow is provided in Figure 1 below. Referring to Figure 1, the chlorine dioxide enters prior to the medium consistency pump (MC) transporting pulp of 12% consistency. Sodium hypochlorite is added less than a second later directly into a dynamic chemical mixer. At high consistency, an air pocket will typically form around the impeller. To avoid this, a degassing pump is installed. Some form of neutralizing chemical for chlorine compounds is fed to the degassing pump, i.e., applied to the gas not to the pulp stream. Both chlorine dioxide and sodium hypochlorite are thoroughly mixed into the pulp prior to an upflow tower of approximately 20 minutes.

The time delay between the two chemicals can affect optical properties other than fluorescence and strategies may be developed to optimize these optical properties in connection with practicing the present invention.

In one embodiment, the reaction of the two chemicals occurs in a single stage. Although a reaction vessel is specified in Figure 1, in other embodiments a pipe can be sufficient, due to the relatively short reaction time needed to practice the invention.

In embodiments of the invention, the pH of the chlorine dioxide/sodium hypochlorite/pulp stream can be adjusted with a pH adjusting chemical (acid, caustic or buffer). In embodiments of the invention, the pH is adjusted to a value in the range of from about 2 to about 7. The specific target pH will generally depend on the system. For example, in a clean system having a fluorescence of about 5, the pH can be in the range of about 2 to about 5, or about 2 to about 4. If the system is heavily buffered, e.g., with calcium carbonate, the pH could be higher, for example in the range from about 4.5 to about 7. Also, the chlorine dioxide charge will lower the pH and sodium hypochlorite charge will increase the pH.

In embodiments of the invention, the temperature of the fluorescence reduction process (the treated pulp slurry) is maintained in the range of about 40°C to about 85°C, or about 65°C to about 80°C.
Although an MC pulp and chemical mixer are used in some embodiments, it is contemplated that some fluorescence reduction will occur regardless of mixing achieved.

It is believed that the application of chlorine dioxide and sodium hypochlorite in tandem requires less chemical to remove fluorescence than either chlorine dioxide or sodium hypochlorite applied individually, and only requires a single stage.

When compared to sodium hypochlorite alone, the process according to the present invention has the added benefit of being able to achieve zero or near-zero fluorescence. It is believed that zero fluorescence is not possible with sodium hypochlorite alone or at least would be very difficult to achieve. Accordingly, in one embodiment of the invention, chlorine dioxide and sodium hypochlorite are added in amounts sufficient and the resulting pulp is maintained under conditions sufficient to achieve a fluorescence of substantially zero or zero. By substantially zero is meant that the fluorescence is 0.25 or less, when measure with a Technidyne Color Touch (CTH-ISO).

When compared to chlorine dioxide alone, the process according to the present invention lowers the chemical charge, while also preventing occurrences of gassing. Gassing is caused by a high level of residual chlorine dioxide at the end of the process and represents a potential danger to workers if inhaled. When chlorine dioxide and sodium hypochlorite are added in combination according to the invention, the residual ClO₂ is reduced, e.g., as much as one-tenth the original amount remains, when maximum fluorescence reduction is desired.

In one embodiment, the fluorescence reduction process is conducted separately from any bleaching or brightening stages, where the goal in bleaching/brightening is to increase brightness and/or whiteness. In such an embodiment, the fluorescence process does not result in an increase in brightness, or only in a relatively small increase in brightness. In embodiments of the invention, the brightness increase as a result of practicing the fluorescence reduction process is less than about 5 ISO, or
less than about 0 ISO. In one embodiment, the fluorescence reduction process is performed before any bleaching or brightening stages.

In embodiments of the invention, the fluorescence reduction process is performed using an upflow tower or a pipe with a residence time of less than about 30 minutes, or less than about 25 minutes, or less than about 20 minutes, after both the chlorine dioxide and sodium hypochlorite have been added to the pulp slurry. In one embodiment, the residence time can be as low as 7 minutes, where good fluorescence reduction results have been observed.

The foregoing general discussion of the present invention will be further illustrated by the following specific but non-limiting examples.

The following examples include evaluating the effect of the time delay for adding the sodium hypochlorite after addition of ClO₂, the effect of separate addition with a long reaction time for ClO₂ alone, the effect of the amount of chemicals added, and the effect practicing the invention on brightness and whiteness of paper.

Example 1

D–H Two-Stage, Thickening between D and H

Pulp was reacted first with chlorine dioxide, then thickened to approximately 25% consistency, diluted to 11% consistency and further treated with sodium hypochlorite. The amount of ClO₂ added was 2.5 kg/ton (1000 kg) of dry pulp and the amount of sodium chlorite was 1.785 kg/ton of dry pulp. Total combined reaction time for both stages was 7 minutes. Previous work showed that after seven minutes the reaction was complete. The chlorine dioxide time was 0, 2, 3.5, and 5 minutes. Zero represents the base case where the two chemicals are added simultaneously. The consistency was 11% and the temperature 71°C for both chlorine dioxide and sodium hypochlorite reactions. The results are shown in Figure 2.

A review of Figure 2 reveals that the fluorescence increased as the sodium hypochlorite addition was delayed, with even as short as a 2 minute delay. Further, once this loss occurred, increased delay had no additional impact on fluorescence.
Paper color can be defined by three coordinates L*, a* and b* in a system called CIELAB, where L* is the lightness, a* is the red-greenness, and b* is the yellow-blueness. These values, as well as other optical properties, were measured as a function of delay in sodium chlorite addition. The effect on L value is shown in Figure 3 and the effect on Tint is shown in Figure 4.

A review of Figures 3 and 4 reveals that brightness, L* value, and whiteness increased in a similar fashion to the fluorescence. These increases were for both the values when ultraviolet was included (UVin) and when ultraviolet was excluded (UVex).

Tint, unlike the fluorescence increased not only with the first delay, but continued to increase for increased delay in sodium hypochlorite addition.

The effect on a and b values is shown in Figure 5. A review of Figure 5 reveals that the delay had little or no effect on a* value, but b* value decreased, and UVin decreased more than the UVex.

**Example 2**

**H-D with no Washing or Thickening Between D and H**

Mixed office waste (MOW) was treated with a combination of chlorine dioxide and sodium hypochlorite in two separate processes. In the first process, chlorine dioxide was mixed with the paper and 5 minutes later sodium hypochlorite was added, followed by further mixing. Total retention time was 20 minutes and the temperature was 71°C.

In the second process, chlorine dioxide was added and allowed to react for 20 minutes alone. Sodium hypochlorite was then added to the paper with no intermediate washing or thickening. Retention time for this stage was also 20 minutes, for a total retention time of 40 minutes. The results are shown in Figure 6.

A review of Figure 6 reveals that despite only having half the retention time, both fluorescence and residual chemical were lower for the first process. The brightness and whiteness were both lower for the D+H process.
**Example 3**

**FR Process – Zero Fluorescence Reduction**

A recycled paper containing mixed office waste with an initial brightness of 89.95 % ISO UV included with a fluorescence of 12.4 was treated with a chlorine dioxide and sodium hypochlorite combination, where the two chemicals were added simultaneously.

The chlorine dioxide charge varied from 0 to 15.5 kg/t, while the sodium hypochlorite was added at 2.9 kg/t and 5 kg/t. The paper was bleached in a constant temperature bath set at 68 C for 15 minutes. The pH was not adjusted and was allowed to float with the reaction. Brightness and fluorescence were measured using a D65 illuminant with a Technidyne Color Touch meter. The results are shown in Figure 7.

A review of Figure 7 reveals that the fluorescence was reduced to less than zero at a chlorine dioxide charge of 6 kg/t when accompanied with 5 kg/t sodium hypochlorite. When the sodium hypochlorite was reduced to 2.9 kg/t, zero fluorescence was not achieved.

The effect of the amount of ClO₂ on pH and residual ClO₂ was measured. The results are shown in Figures 8 and 9.

A review of Figures 8 and 9 reveals that the ClO₂ residual was less than 0.01 gpl for both charges of sodium hypochlorite. Additional sodium hypochlorite also served to increase the pH from 3.2 to 4.5 at a fluorescence of 0.5.

**Example 4 –**

**D→H Single Stage, No Thickening or Washing between D and H**

Recycled paper was reacted in a single stage with chlorine dioxide and sodium hypochlorite. The sodium hypochlorite addition was varied by 0, 2, 5, 10, 15 and 18 minutes, where zero represents simultaneous addition (base case). No washing or thickening took place between the two chemicals. The total retention time was 20 minutes for all runs; the consistency was 11% and the temperature 71.1°C. The effect
on brightness and whiteness were evaluated as a function of time delay in adding the sodium hypochlorite. The results are shown in Figures 10 and 11.

A review of Figure 10 reveals that all runs had fluorescence of between 1.6 and 2.1. Although the spread of the data appears significant, most points had lower fluorescence than the base case indicating the delay had either no detrimental effect or only a minor detrimental effect.

A review of Figures 10 and 11 further reveals that the brightness and whiteness increased for both UVin and UVex with the initial delay in sodium hypochlorite addition of 2 minutes, and the tint also increased for the first delay. All parameters remained relatively constant for increased sodium hypochlorite delay.
What is claimed is:

1. A method for reducing fluorescence in recycled pulp, said method comprising:
   a) contacting a pulp slurry containing fluorescent agents with chlorine dioxide;
   b) contacting said pulp slurry with sodium hypochlorite sodium component chosen from sodium hypochlorite, at least one sodium hypochlorite derivative or combinations thereof, in an amount sufficient to reduce the fluorescence of said pulp;
   wherein the pulp is contacted with said sodium hypochlorite component simultaneously with or after contact with chlorine dioxide.

2. The method according to claim 1, wherein the pulp is contacted with said sodium hypochlorite component less than about 2 minutes after contact with the chlorine dioxide.

3. The method according to claim 2, wherein the pulp is contacted with said sodium hypochlorite component less than about 30 seconds after contact with the chlorine dioxide.

4. The method according to claim 3, wherein the pulp is contacted with said sodium hypochlorite component and chlorine dioxide simultaneously.

5. The method according to any one of claims 1-4, wherein the amount of said chlorine dioxide component contacted with the pulp is in the range from about 4 to about 15 kg/t (1000 kg) of dry pulp.

6. The method according to any one of claims 1-5, wherein the amount of said sodium hypochlorite component contacted with the pulp is in the range from about 2 to about 12.5 kg/t (1000 kg) of dry pulp.

7. The method according to any one of claims 1-6, wherein the weight ratio of chlorine dioxide to said sodium hypochlorite component is in the range from 1:1 to 3:1.

8. The method according to any one of claims 1-7, wherein the weight ratio of chlorine dioxide to said sodium hypochlorite component is in the range from 1.2:1 to 1.8:1.
9. The method according to any one of claims 1-8, wherein the pulp slurry has a consistency in the range of about 4% to about 20% prior to contacting with the chlorine dioxide.

10. The method according to any one of claims 1-9, further comprising adding a pH adjusting chemical in an amount to adjust the pH of the pulp slurry to a value in the range of from 2 to 7.

11. The method according to any one of claims 1-10, wherein the sodium hypochlorite component is sodium hypochlorite.
**FIGURE 1**

**FIGURE 2**

*Figure 2: ClO₂ Effect on Fluorescence Value*

**Time Before Sodium Hypochlorite Addition, min.**

- Bright UVin
- Bright UVex
- FI

**Fluorescence, D65 ISO**

- 0.0
- 1.0
- 2.0
- 3.0
- 4.0
- 5.0

**Brightness, ISO**

- 70
- 72
- 74
- 76
- 78
- 80
- 82
- 84
FIGURE 7

Figure 7: Effect of ClO₂ on Fluorescence
(C Illuminant)

- F1 H = 0.5 % on stock
- F1 H = 0.29 % on stock

Initial Pulp Brightness
UVin = 89.85 %ISO
UVex = 77.48 %ISO
FI = 12.37

FIGURE 8

Figure 8: Effect of ClO₂ on pH and Residual
(NaOCl = 0.29%)

- Final pH
- Residual, gpl

Chlorine Dioxide, % on stock
FIGURE 9

Figure 9: Effect of ClO₂ on pH and Residual
(NaOCl = 0.5%)

Final pH
Residual, gpl

FIGURE 10

Figure 10: ClO₂ Effect on Fluorescence

Brightness, ISO UV/in
Fluorescence, ISO

Bright. UV/in
FI
FIGURE 11

Figure 11: ClO₂ Effect on Optical Value

Whiteness, ISO UVIn

Tint, ISO

Sodium Hypochlorite, min.