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**④ OZONE BLEACHING OF CELLULOSIC MATERIALS.**

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| <p>⑩ Priority: <b>24.06.82 US 391747</b></p> <p>⑪ Date of publication of application:<br/><b>04.07.84 Bulletin 84/27</b></p> <p>⑫ Publication of the grant of the patent:<br/><b>12.11.86 Bulletin 86/46</b></p> <p>⑬ Designated Contracting States:<br/><b>FR GB SE</b></p> <p>⑭ References cited:<br/><b>US-A-2 161 045</b><br/><b>US-A-3 806 404</b><br/><b>US-A-3 920 547</b><br/><b>US-A-4 008 120</b><br/><b>US-A-4 230 571</b></p> <p><b>Tappi J. Techn. Ass. Pulp Paper Ind., vol. 60, no. 9, September 1977 (Atlanta, GA, US), L.D. Markham et al. "The effect of ultraviolet light on the chlorine dioxide bleaching of kraft pulp", see pages 138-140</b></p> | <p>⑮ Proprietor: <b>SCOTT PAPER COMPANY</b><br/><b>Industrial Highway Tinicum Island Road Tinicum Township Delaware County, PA 19113 (US)</b></p> <p>⑯ Inventor: <b>SINGH, Rudra P.</b><br/><b>4404 Chandler Drive Brookhaven, PA 19015 (US)</b></p> <p>⑰ Representative: <b>McCall, John Douglas et al</b><br/><b>W.P. THOMPSON &amp; CO. Coopers Building Church Street Liverpool L1 3AB (GB)</b></p> <p>⑱ References cited:<br/><b>Chemical Abstracts, vol. 96, no. 22, 31 May 1982 (Columbus, OHio, US) K.D. Mgaloblishvili et al.: "Device for ozone decomposition", see page 160, left-hand column, abstract no. 183687d, SU, A, 895923, 7 January 1982</b></p> |
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## Description

### Background of the invention

#### Field of the invention

Bleaching lignocellulosic material with ozone. 5

### Brief summary of the invention

It has been found that, during pulp bleaching with ozone, irradiation of the pulp with ultraviolet light enhances the efficiency of the ozone and the bleachability of the pulp. 10

### Detailed description of the preferred embodiment

The following definitions will be used in this application. 15

Pulping is the changing of wood chips or other lignocellulosic material to fibrous form. Chemical pulping requires cooking of such material in solution with a chemical, and includes partial removal of the coloring matter such as lignin associated with the wood. 20

Bleaching is the treatment of cellulosic fibers to remove or alter the coloring matter associated with the fibers to allow the fiber to reflect white light more truly. 25

The present invention is concerned with the degradation of lignin and hence "delignification" and "bleaching" are used interchangeably.

Consistency is the weight of pulp fibers in a pulp suspension usually expressed as a percentage. For example, one part by weight oven dry fiber in one hundred parts by weight of a mixture of water and fibers would be a pulp suspension of 1% consistency. The consistency of the pulp will depend upon the type of dewatering equipment used. 30

The following definitions of consistency are based on the use of those terms in "The Bleaching of Pulp", Third Edition, Revised, edited by the present inventor, TAPPI Press 1979, pages 243—246. 35

Low consistency is typically from 4—6%. It is a suspension that is pumpable in an ordinary centrifugal pump and is obtainable using deckers and filters without press rolls. 40

Medium consistency is between 10 and 15%. This consistency can be obtained by vacuum washers and vacuum thickeners. Above 15%, press rolls are needed for dewatering. A medium consistency slurry is pumpable by special machinery. 45

High consistency is from 20—35%. This consistency is obtained by the use of presses. High consistency pulp is essentially nonpumpable.

One measure of the efficacy of a bleaching process is the degree of delignification. There are many methods of measuring the degree of delignification of the pulp, but most are variations of the permanganate test. 50

The permanganate test used herein provides a Kappa number—a measure of potassium permanganate solution consumed by oven dry pulp under specified conditions. The Kappa number is determined in accordance with TAPPI standard test method T 214 M42. 55

A fairly length recitation of prior art literature and patent references describing gas phase ozone bleaching of lignocellulosic materials is contained in U.S. Patent 4,080,249 to Kempf et al column 1, lines 31—46. These references disclose the ozone bleaching of pulp at low, medium and high consistencies. Therefore, "ozone bleaching" as used herein is not to be limited to any particular consistency but may be employed at whatever consistency is preferred as suitable apparatus is already known for all three levels. For low and medium consistency pump, i.e. pumpable slurries, a photoreactor such as disclosed for example in U.S. Patent 3,637,342 to Veloz can be employed, following the teachings of Kempf et al for entraining the ozone bearing gas into the slurry of pulp. For high consistency pulp reactors, such as disclosed by Fritzvold in U.S. Patents 4,278,496 and 4,123,317 and by Carlsmith in U.S. Patents 3,814,664 and 3,964,962 it is contemplated that lamps emitting ultraviolet light be mounted on the walls of the reaction chamber. 60

The use of ultraviolet light and ozone together in a process for the destruction of cyanide in an aqueous cyanide solution has been disclosed in US—A—3,920,547 and in a process for purification of water in US—A—4,230,571. Neither of these citations however discloses use of ozone and ultraviolet light in bleaching lignocellulosic pulp nor suggests any such method and thus does not comment upon the problems of bleaching lignocellulosic pulp. 65

In accordance with the present invention, ultraviolet radiation increases the effectiveness of the ozonation. Without wishing to be bound by theory, the present inventor believes that the ultraviolet radiation electronically excites the lignin in the material to be bleached. The excited lignin may then form a high energy complex with the ozone (or possibly singlet oxygen). It is speculated that this complex immediately breaks apart into degradation products of lignin. Lignin, because of its aromatic nature, absorbs strongly in the ultraviolet region of the spectrum. The typical lignin absorption spectrum comprises a maximum at 205 nm (nanometers), a less intense peak at 280 nm, with less significant shoulders in the spectrum at 250, 300 and 360 nm.

In reducing the present invention to practice, pump was subjected to treatment with ozone carried in oxygen while being irradiated at the aforementioned frequencies of ultraviolet light. A 360 watt spectrophotometer was used as the source of ultraviolet. Samples of pulp weighing 0.1 gram each (oven dried basis) were irradiated in a closed chamber consisting of two glass cells for a period of two hours. The cells were partially covered with reflective foil so as to increase the energy available to the pulp. In the data which follows the reduction in K number (increase in brightness) is on the order of two, which—given the low power of the spectrophotometer—is considered to be significant and having the potential to be translated to pilot or commercial scale apparatus. 65

Sample	K number
Ultrated pulp	18.324
Ozonated pulp	17.389
Ozonated and irradiated at 205 nm	15.044
250 nm	15.278
280 nm	15.672
300 nm	15.586
360 nm	15.789

At each of these wave lengths which are characteristic of the absorption spectrum of lignin, the ultraviolet radiation increased the effectiveness of the ozonation. As may be seen, light at 205 nm had the greatest effect. While commercially available light sources for photo-reactors do not generally emit a single wavelength, it will be sufficient if some of the light is at one or more of the more effective frequencies. Moreover, it is desirable to choose wavelengths at which cellulose does not absorb. By irradiating at absorption peak characteristic to lignin and not to cellulose, the lignin can be made more susceptible to attack by ozone than the cellulose thus tending to cause the ozone to react preferentially with lignin and tending to cause less degradation of cellulose.

While the present invention has been described in terms of a laboratory reduction to practice, it will be appreciated by one of ordinary skill in the art having the benefit of the teachings contained herein that the invention as defined by the appended claims is applicable to various types of reaction vessels already known in the art.

#### Claims

1. A process for bleaching lignocellulosic pulp with ozone, characterized by irradiating said pulp with ultraviolet light while mixing an ozone bearing gas with the pulp.

2. A process as claimed in claim 1, characterized

in that said ultraviolet light contains frequencies corresponding to the absorption peaks characteristic of lignin.

3. A process as claimed in claim 2, characterized in that the frequency of said ultraviolet light is in the range of 205 nm to 360 nm.

4. A process as claimed in claim 3, characterized in that the ultraviolet light is concentrated at a frequency of 205 nm.

#### Patentansprüche

1. Verfahren zum Bleichen von Lignocellulosepulpe mit Ozon, dadurch gekennzeichnet, daß die Pulpe mit Ultraviolettlicht bestrahlt wird, während ein ozonhaltiges Gas mit der Pulpe vermischt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Ultraviolettlicht Frequenzen aufweist, die den für Lignin charakteristischen Absorptionsspeaks entsprechen.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die Frequenz des Ultraviolettlichts in einem Bereich zwischen 205 nm und 360 nm liegt.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Ultraviolettlicht bei einer Frequenz von 205 nm gebündelt wird.

#### Revendications

1. Un procédé pour blanchir par l'ozone une pâte lignocellulosique, caractérisé par le fait qu'on irradie ladite pâte par de la lumière ultraviolette tout en mélangeant un gaz porteur d'ozone à la pâte.

2. Un procédé tel que revendiqué dans la revendication 1, caractérisé par le fait que ladite lumière ultraviolette contient des fréquences correspondant aux pics d'absorption caractéristiques de la lignine.

3. Un procédé tel que revendiqué dans la revendication 2, caractérisé par le fait que la fréquence de ladite lumière ultraviolette se situe dans la plage de 205 nm à 360 nm.

4. Un procédé tel que revendiqué dans la revendication 3, caractérisé par le fait que la lumière ultraviolette est concentrée à une fréquence de 205 nm.

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