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BLEACHING METHOD

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This invention relates to improvements in the bleaching of cellulosic materials, and more particularly to the bleaching of materials composed primarily of cellulose or of cellulose derivatives.

In the conventional methods of bleaching cellulosic materials, the most commonly used reagents have been chlorine and hypochlorites. While the use of these reagents under varying conditions produces a satisfactory degree of bleaching, these compounds at the same time tend to exert a destructive action upon the cellulosic material itself when any attempt is made to secure a substantial degree of bleaching. As a result of this tendency to attack the fiber many complicated multi-stage processes have been proposed, all of which involve very critical control and few of which, if any, have successfully met the problem of producing an advanced degree of whiteness without substantial degradation of the fiber.

I have discovered a particularly advantageous method of bleaching cellulosic materials which avoids the disadvantage of degradation and loss of the cellulosic material attendant upon the use of the usual bleaching agents. The process of the present invention also avoids the necessity for rigorous and critical control necessary in the heretofore employed methods. I have found that cellulosic material may be successfully bleached to any desired degree of whiteness without damage to the fiber by suspending the cellulose in an alkaline solution and introducing therein chlorine dioxide which I have found to be a peculiarly efficient bleaching agent with respect to the colored compounds commonly associated with cellulosic materials.

It has previously been proposed to employ chlorine dioxide for the bleaching of colored organic solutions and compounds. Such proposals have, however, involved the use of chlorine dioxide in neutral or acid aqueous solutions. The success of processes based on this method of procedure has been limited due in part to the difficulty of causing sufficient ClO_2 gas to dissolve in the aqueous solution. I have found that in an alkaline solution the ClO_2 is readily absorbed and very effectively oxidizes the colored bodies associated with the cellulose without attacking the cellulose itself. In such an oxidation the chlorine dioxide undergoes a limited reduction. In the alkaline solutions which I employ in the process of the present invention, the ClO_2 undergoes a partial reduction to chlorite ion as a result of the action of the oxidizable coloring matter. This reaction thus provides a further ad-

vantage in the present process in that chlorite, a valuable product in itself, is produced concurrently with the bleaching of the cellulosic material. Substantially no chlorate is formed as distinguished from the equimolecular formation of chlorite and chlorate in the simple absorption of chlorine dioxide in an alkaline medium.

The bleaching operation of this invention is applicable to cellulosic materials generally and the term "cellulosic materials" as used herein has such a broad significance. The invention is useful, for example, in bleaching paper and paper pulp including sulphite and kraft pulp, pulped wood, cotton linters, hemp, and cellulose derivatives such as rayon.

The alkaline solution used in my process may be an aqueous solution of the alkali metal or alkaline earth metal oxides or hydroxides. An aqueous solution of an alkali metal carbonate such as, for example, soda ash may also be used with advantage. In operations in which the less soluble of the oxides or hydroxides are employed such as, for example, a solution of lime, a suspension of the alkaline substance is usually employed. While alkaline materials such as carbonates or bicarbonates or other soluble alkaline salts may successfully be employed, I prefer, in general, to use the oxides or hydroxides of the metals of the above referred to class. I use the term "free base" herein to designate such soluble oxides and hydroxides as distinguished from other alkaline materials.

The limits of concentration of the alkaline materials which may be used in the present process vary over a wide range. I prefer, however, to operate with an alkaline solution whose pH does not substantially exceed a value of about 13.

The desired degree of bleaching on a given cellulosic material may be attained directly by the reduction of chlorine dioxide as above described. In certain cases, however, it may be advantageous to use this ClO_2 reduction as one step in a multi-stage bleaching operation. Thus, the bleaching operation may be initiated by means of any conventional bleaching agent such as, for example, chlorine or hypochlorite, and completed by the present process. In a case such as this the incomplete bleaching by means of the chlorine or hypochlorite should be stopped at a point prior to the inception of degradation of the fiber. By such a combination process important economies may be realized.

A further multi-stage bleaching operation possessing marked advantages over known procedures involves the completion of the bleaching

operation by means of chlorine dioxide in an alkaline solution as herein described, the precedent bleaching having been accomplished in an acidified chlorite solution. In this manner a highly advantageous cyclic operation may be developed in which the chlorite solution of an alkali metal or alkaline earth metal produced as a result of the reduction of chlorine dioxide by the coloring matter in the cellulose may be activated by acidification and used in the initial stages of the bleaching of a subsequent batch of cellulose. A similar combined operation may be developed in which the chlorite solution resulting from a previous bleaching step may be activated by means of chlorine, in which case the chlorine appears to oxidize the chlorite back to chlorine dioxide rather than reacting directly on the cellulose with the consequent degradation. In such a process the thus produced chlorine dioxide serves to bleach the coloring matter in a manner similar to that described above for the use of ClO_2 alone.

The bleaching operation of my invention may be carried out over a wide range of temperature. The bleaching proceeds with sufficient rapidity at ordinary temperatures or at moderately elevated temperatures to permit substantial savings in heat and in the time required for heating as compared to operations requiring substantially elevated temperatures. Since acidified solutions are not employed in the present process and since operation at high temperatures is not essential, many problems of corrosion of equipment which accompany many bleaching operations are thus eliminated.

The present bleaching operation is particularly advantageous in the bleaching of cellulosic materials such as, for example, kraft pulp where the requirements for strength of fiber are especially rigorous. The following will serve as a typical example of the operation of my invention on such a pulp: Kraft pulp is uniformly suspended in an aqueous solution of sodium hydroxide having a pH of 9.5-13. Chlorine dioxide is passed into the solution in a manner adapted to secure efficient absorption of the gas in the solution. The reaction is conducted at room temperature. The kraft pulp attains a high white color with no loss or weakening of the fiber.

The chlorine dioxide may be introduced into the alkaline solution in my process by means of a water solution containing chlorine dioxide or by passing chlorine dioxide gas directly into the solution.

The following examples will serve to illustrate the above referred to embodiment of my invention in which the bleaching by means of chlorine dioxide in alkaline solution is the final step:

Example I

50 parts (by weight) of sulphite pulp which had been treated with 3½% chlorine, neutralized with lime, and washed with water was suspended in water so that the final consistence of the pulp was 5%. This suspension was then treated with a chlorite solution extracted from the last stage of a previous bleach which contained 1.3% of available chlorine on the weight of the pulp, and the entire solution was adjusted to a pH of 4. After standing overnight at room temperature the pulp was removed from this solution, washed with water, and again suspended in water, which contained 3 parts of lime, to produce a suspension of a consistency of 5%. Air carrying a low concentration of chlorine dioxide was passed into the pulp for a period of 45 mins. The bleached pulp was removed from this solution and washed.

The pulp had attained a high degree of whiteness with no apparent loss of strength or degradation of fiber.

Example II

100 parts (by weight) of kraft pulp which had been treated with 10% chlorine followed by lime neutralization and washing with water, was suspended in a chlorite solution secured in the final stage of a previous bleaching, and containing 2.2 parts of available chlorine. The whole solution was adjusted to a pH of 4 with hydrochloric acid and warmed to a temperature of 60° C. during a period of 30 mins. The pulp was maintained at this temperature for 3½ hours. The pulp was then removed from this solution, washed, and suspended to produce a suspension of 5% consistence in a solution containing sodium hydroxide. Chlorine dioxide was passed into the solution at a temperature of 40° C. over a period of 1 hr. After standing for another period of 1 hr. the pulp was removed from the solution and washed. The pulp had attained a high degree of whiteness with no degradation or loss of fiber.

I claim:

1. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the cellulosic material to be bleached in an aqueous alkaline solution having distributed therethrough an inorganic alkaline material of substantial solubility of the class consisting of the alkali metal and alkaline earth metal oxides, hydroxides, and carbonates, introducing chlorine dioxide into said aqueous solution, and removing the bleached cellulosic material from the solution.

2. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the cellulosic material to be bleached in an aqueous alkaline solution having distributed therethrough an inorganic alkaline material of substantial solubility of the class consisting of the alkali metal and alkaline earth metal oxides, hydroxides and carbonates, introducing gaseous chlorine dioxide into said aqueous solution, and removing the bleached cellulosic material from the solution.

3. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the cellulosic material to be bleached in an aqueous medium having distributed therethrough a free base chosen from the class consisting of the alkali metal and alkaline earth metal oxides and hydroxides, introducing gaseous chlorine dioxide into said solution, and removing the bleached cellulosic material from the solution.

4. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the cellulosic material to be bleached in an aqueous solution of sodium hydroxide, introducing chlorine dioxide into said aqueous solution, and removing the bleached cellulosic material from the solution.

5. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the cellulosic material to be bleached in an aqueous solution of soda ash, introducing chlorine dioxide into said aqueous solution, and removing the bleached cellulosic material from the solution.

6. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the cellulosic material to be bleached in an aqueous suspension of lime, introducing chlorine dioxide into said

aqueous solution, and removing the bleached cellulosic material from the solution.

7. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending an incompletely bleached cellulosic material to be bleached in an aqueous alkaline solution having distributed there- through an inorganic alkaline material of sub- 5 stantial solubility of the class consisting of the alkali metal and alkaline earth metal oxides, 10 hydroxides, and carbonates, introducing chlorine dioxide into said aqueous solution, and remov- ing the bleached cellulosic material from the so- lution.
8. The method of bleaching cellulosic mate- 15 rials without substantial degradation of the fiber

which comprises suspending in an aqueous alka- line solution having distributed therethrough an inorganic alkaline material of substantial solu- bility of the class consisting of the alkali metal and alkaline earth metal oxides, hydroxides, and 5 carbonates, a cellulosic material which has been partially bleached by being suspended in an acid solution of a chlorite of the class consisting of the chlorites of the alkali metals and alkaline 10 earth metals, introducing chlorine dioxide into said aqueous alkaline solution, removing the com- pletely bleached cellulosic material from the so- lution, and returning the thus formed chlorite 15 solution to the initial acid bleaching stage of a further quantity of cellulosic material.

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