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METHOD OF BLEACHING

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This invention relates to improvements in the bleaching of cellulosic material and, more particularly, to a method of bleaching materials composed of cellulose or cellulose derivatives such as, for example, kraft or sulfite pulps, to a desired whiteness without substantial degradation of the material being bleached.

In the conventional methods of bleaching cellulosic materials, chlorine has been a commonly used reagent. While the use of this reagent under varying conditions, most frequently in conjunction with hypochlorites in various multi-stage processes, will produce a satisfactory color, its use involves a strong tendency to attack the cellulosic material itself. This tendency is particularly marked in cases where a high degree of bleaching is required. In attempting to overcome this deleterious effect, many complicated multi-stage processes have been proposed, all of which involve very rigorous and critical control and few of which, if any, have successfully met the problem of producing an advanced degree of whiteness without substantially degrading the fiber. The strong oxidizing power of chlorine and the hypochlorites, and also the tendency of chlorine to react directly with the cellulosic material, are apparently the cause of this usually encountered degradation and loss of material. This tendency has been particularly troublesome in the bleaching of kraft or sulfate pulps where strength of fiber is of paramount importance. As a consequence it has been necessary to sacrifice color in order to prepare a kraft product meeting the strength requirements imposed by the trade.

I have discovered a particularly advantageous method of bleaching cellulosic materials in which the oxidizing power of chlorine is utilized in the bleaching of the colored bodies associated with the cellulosic materials, but in which the cellulose itself is not destroyed or its strength substantially impaired. The process of the present invention has the additional advantage that the necessity for the rigorous and critical control of reaction conditions and proportions of reagents attendant upon the heretofore proposed bleaching methods, which involve the use of chlorine, is avoided. In accordance with my process, cellulosic materials may be successfully bleached to any desired degree of whiteness, without damage to the fiber, by suspending the material to be bleached in an aqueous medium and introducing therein a mixture of chlorine and chlorine dioxide. While the said mixture of gases may be introduced into the suspension in the form of an aque-

ous solution, I prefer to effect its introduction by passing a gaseous mixture containing these two gases into the aqueous suspension.

It has previously been proposed to employ chlorine dioxide for the bleaching of colored organic solutions and compounds. In a co-pending application Serial No. 163,695, filed September 13, 1937, and which issued as United States Patent No. 2,129,719, September 13, 1938, I have described and claimed a process which involves the introduction of chlorine dioxide into an aqueous suspension of a cellulosic material having an alkaline material distributed therethrough. In this process, the ClO_2 is particularly effective in bleaching the colored bodies associated with the cellulose but does not degrade or destroy the cellulose itself.

In the bleaching of cellulosic materials, a given quantity of material possesses a certain "bleach demand" which must be satisfied in order to impart to the material a specified degree of whiteness. In cases in which the oxidation or chlorination of the colored bodies to form colorless substances is accomplished by compounds containing chlorine, the "bleach demand" is frequently calculated in terms of available chlorine introduced into the system by the bleaching agent. In the above referred to process, the total required quantity of available chlorine is supplied by ClO_2 . In accordance with the present invention, however, varying proportions of the available chlorine necessary to meet the "bleach demand" are introduced in the form of chlorine. In direct contrast to previously known methods of using chlorine in bleaching, its use in the instant process does not involve damage to the fiber. In my process, in which a mixture of chlorine and chlorine dioxide is employed, the customary destructive action of chlorine either does not exist or is negligible. The use of chlorine under such conditions possesses numerous advantages particularly with respect to the cost of operation when compared to an operation in which the total required available chlorine is supplied by ClO_2 . Chlorine is more readily obtainable than chlorine dioxide and, further, the preparation of ClO_2 , free from Cl_2 , usually involves undesirable supplementary operations. In my process, ClO_2 , which contains Cl_2 incident to its preparation, not only may be used, but Cl_2 may even be added to such a mixture to increase its chlorine content.

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 sulfite and kraft or sulfate pulp, pulped wood, cotton linters, hemp and cellulosic derivatives such as rayon.

In carrying out my process, a mixture of Cl_2 and ClO_2 , for example a gaseous mixture of the two which may be diluted with an inert gas such as air, is introduced into an aqueous suspension of the cellulosic material, generally referred to in bleaching operations as the pulp. Depending on the conditions of operation, and the nature of the cellulosic material, considerable latitude is permissible in the relative proportions of ClO_2 and Cl_2 which may be used in my process. One advantageous source of a mixture containing ClO_2 and Cl_2 is a generator containing a chlorate, NaClO_3 or $\text{Ca}(\text{ClO}_3)_2$, for example, which is acidified with an acid, HCl or H_2SO_4 , for example. Such a method of producing a ClO_2 - Cl_2 gas mixture is described in my two co-pending applications Serial Numbers 85,667 and 85,668, both filed June 17, 1936. Depending on the conditions of acidification, the relative proportions of ClO_2 and Cl_2 from such a generator will vary considerably. In the present process, I have found that gas mixtures having a ClO_2 : Cl_2 ratio between 1:1 and 2:1 are particularly advantageous. These limits, however, are not critical and mixtures containing a higher ratio of chlorine dioxide, for example 3.5:1, or a higher ratio of chlorine, may be employed. The present bleaching operation is not restricted to mixtures obtained from such a generator, but mixtures obtained from any source, or prepared by enriching such a generator mixture with respect to either component by adding one of the compounds from an outside source, are suitable.

The aqueous suspension of the cellulosic material prepared as the first step in my process may vary over wide limits with respect to its hydrogen ion concentration, there apparently being no marked criticality attached to the pH of the aqueous medium provided that it is not excessively acid or alkaline. My process operates successfully at pH values below 7 but, in general, I prefer to operate with pulp solutions on the alkaline side of neutrality and particularly those having a pH between 7 and 10. The continued introduction of chlorine tends to develop acidity in the solution as a consequence of which, in some cases, it is preferable to introduce regulated quantities of an alkaline material during the course of the chlorine addition to prevent the development of excessive acidity. This is not a requisite, however, since, in many cases, sufficient free alkali may be added at the start to prevent the solution becoming excessively acid or a buffer salt, either alkaline or acid, may be employed to accomplish the same result. The alkaline materials appropriate for this purpose may be any of a number of "free bases" or alkaline salts, including alkaline buffer salts. The "free bases" include the alkali metal and alkaline earth metal oxides and hydroxides, sodium hydroxide and calcium oxide or hydroxide being particularly useful in commercial operations. Other alkaline compounds, such as the alkali metal carbonates or bicarbonates, soda ash for example, may also be used. A compound such as calcium carbonate is also suitable and may be employed by suspending an appropriate amount in the pulp suspension at the start of the operation. As the chlorine is introduced, such an insoluble compound is gradually used up in neutralizing the acids formed by the chlorine, and an

acidity capable of harming the fiber or of interfering with the bleaching operation is thus prevented. Among the buffer salts which function successfully in my process may be mentioned the borates, the alkali phosphates and certain soluble calcium salts such as the acetate, cyanide, fluosilicate, lactate and salicylate.

The bleaching operation of my invention may be carried out over a wide range of temperature. The bleaching proceeds with sufficient rapidity, however, at ordinary temperatures or at moderately elevated temperatures, thus obviating the necessity for heating large volumes of pulp in order to produce a satisfactory speed of reaction. Depending somewhat on the material being bleached, the relative proportion of chlorine in the gas mixture and the alkalinity of the solution, the temperature of the pulp is, in some instances, advantageously moderately elevated, for example, to a temperature of about 60°C . Such an increase is frequently desirable in view of the increased speed of reaction resulting therefrom.

As previously stated, chlorine is employed in the present process but its use is not accompanied by the degradation of the fiber which is considered typical of the use of this gas in bleaching. I am unable to explain definitely the reason for this although certain postulated mechanisms given below appear to provide a satisfactory explanation. Whatever the correct explanation may be, however, I have found that the introduction of chlorine, together with chlorine dioxide, into an aqueous solution, in which is suspended a cellulosic material, effects a bleaching of the cellulose without degradation. Such an action is characteristic of chlorine dioxide rather than of chlorine.

Comparative experiments have been conducted on kraft pulp which demonstrate the relative action of chlorine, chlorine dioxide, and of a mixture of chlorine and chlorine dioxide. In one specific instance, a kraft pulp was bleached to a color of 78 measured by the Reflectometer Method as proposed by the Institute of Paper Chemistry and recorded as "brightness", by introducing chlorine into a pulp having a pH of 9.3. In attaining this color, however, the strength of the fiber was damaged to an extent of nearly 50%, an equivalent degradation or greater being encountered when solutions of other pHs both above and below this value were used. In other tests, in which chlorine dioxide was the bleaching agent and in which a brightness of 78 was attained, there was no appreciable degradation of the fiber. Further tests, in which mixtures of chlorine dioxide and chlorine were employed to obtain comparable degrees of bleaching, and in which pulp suspensions having varying pH values were used, demonstrated that, in these cases, the introduction of chlorine produced no substantial degradation of the fiber whereas, when chlorine was used alone, the degradation was marked. The following will serve as an illustrative example of a bleaching operation in which a chlorine dioxide-chlorine mixture was used as the bleaching agent.

Example I

Kraft pulp, in the form of wet crumbs, was suspended in a sulfate buffered solution having a pH of 7.3. 125 grams of pulp, on a dry basis, were suspended in $2\frac{1}{2}$ liters of solution in this experiment. A mixture of chlorine dioxide and chlorine, having a mole ratio of ClO_2 : Cl_2 equal to 1.6, was passed into 400 cc. of water until the solution contained 2.12 grams of available chlorine. This solution was added to the pulp suspension

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and the mixture maintained at a temperature of 60° C. for one hour with stirring. The pulp was then filtered and washed, the filtrate containing 5% of unreacted available chlorine. The strength of this pulp was 134% Mullen compared to 141% for the original unbleached pulp. The color of the pulp was 75 measured on the G. E. Brightness Tester as compared to 55.7 at the beginning of the operation.

In a similar experiment involving an application of the bleaching process of my invention, using a kraft pulp suspended in an aqueous solution buffered to a pH of 9.3 by a borate buffer, and using a gas mixture having a molar ratio of ClO_2 to Cl_2 of 3.05, the same degree of bleaching was attained with an equally small fiber degradation when measured by the same methods.

Certain variations in the heretofore described method of procedure are possible, in accordance with my process, particularly when the solution is maintained in an alkaline condition. For example, instead of achieving the desired degree of bleaching on a given cellulosic material directly, by treatment with a mixture of chlorine dioxide and chlorine, it may be advantageous, in certain cases, to use such a treatment as the second step in a two-step bleaching operation. Thus, the bleaching 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. Another variation in the process depends upon the fact that, when bleaching in an alkaline solution with chlorine dioxide, the ClO_2 is reduced to a chlorite. Chlorite itself is an efficient bleaching agent for cellulosic materials and bleaches with particular efficiency when the solution is acidified. Thus, in the process of the present invention, the chlorite remaining in the solution as the result of the reduction of the chlorine dioxide may be utilized to complete the bleaching, thereby making possible the use of a lesser quantity of ClO_2 . An example of the application of both of the just-described possible variations in my process is as follows:

Example II

100 grams of sulfite pulp were treated with 3½ grams of chlorine in a dilute aqueous suspension. The pulp was neutralized with lime and washed. The pulp was then adjusted to a consistency of 5% and 5 grams of calcium oxide added thereto. A gaseous mixture of chlorine dioxide and chlorine was generated by slowly dropping a mixture of 13 cc. of concentrated HCl and 7 cc. of water into a solution of 10 grams of sodium chlorate in 10 cc. of water. An air stream was used to facilitate the transfer of the chlorine-chlorine dioxide mixture into the pulp suspension. At the end of two hours the chlorine introduced into the pulp had disappeared and the pulp was then acidified and allowed to stand for a second two-hour period during which further bleaching occurred as a result of the action of the chlorite resulting from the reduction of the chloride dioxide.

As previously stated, I am unable to explain why chlorine may be used in the bleaching process of my invention without causing a degradation of the cellulosic material. As a hypothesis for the mechanism of the reactions which may take

place, however, I believe that the reaction involved depends ultimately on the bleaching power of chlorine dioxide. As previously pointed out, chlorine dioxide will bleach cellulosic material in an alkaline medium with the production of an equimolar quantity of chlorite. It is further known that chlorine dioxide may be produced by introducing chlorine into a solution of a soluble chlorite, a reaction which produces one mole of ClO_2 for each mole of chlorite reacted. It seems probable, therefore, that there are here involved consecutive reactions having widely varying reaction rates. If such is the case, a sufficient quantity of chlorite may be produced by the reduction of ClO_2 occurring as a result of its bleaching action to react with the added chlorine to produce further quantities of chlorine dioxide all before the chlorine has a sufficient opportunity to react directly with the cellulosic material. In the cases where the operation is not conducted in an alkaline medium, it may be postulated that an intermediate chlorine compound, Cl_2O_3 , the anhydride of chlorous acid, will form and be immediately oxidized back to chlorine dioxide by the added chlorine. Whatever the explanation or the mechanism may be, however, the present process permits the use of substantial proportions of chlorine in a bleaching operation whereby the oxidizing capacity of the chlorine is made use of but without the usually resultant attack on the material being bleached.

I claim:

1. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium and introducing a mixture of chlorine and chlorine dioxide into the aqueous suspension.
2. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium and introducing into the aqueous suspension a gaseous mixture containing chlorine and chlorine dioxide.
3. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium having distributed therethrough an alkaline material, and introducing a mixture of chlorine and chlorine dioxide into the aqueous suspension.
4. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium having distributed therethrough an inorganic alkaline material, and introducing into the aqueous suspension a gaseous mixture containing chlorine and chlorine dioxide.
5. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium having distributed therethrough an inorganic alkaline material of the class consisting of the alkali metal and alkaline earth metal oxides, hydroxides and carbonates, and introducing into the aqueous suspension a gaseous mixture containing chlorine and chlorine dioxide.
6. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium having distributed therethrough an inorganic alkaline material of the class consisting of the alkali metal and

alkaline earth metal oxides, hydroxides and carbonates in an amount suitable to maintain an alkalinity in the pulp solution between pH=7 and pH=10, and introducing into the aqueous suspension a gaseous mixture containing chlorine and chlorine dioxide.

7. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium having dissolved therein an alkaline buffer salt in an amount suitable to maintain an alkalinity in the pulp solution between pH=7 and pH=10, and introducing into the solution a gaseous mixture containing chlorine and chlorine dioxide.

8. The method of bleaching cellulosic materials without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium having distribut-

ed therethrough an inorganic alkaline material, and introducing into the aqueous suspension a gaseous mixture containing chlorine and chlorine dioxide in which the $\text{ClO}_2:\text{Cl}_2$ ratio is within the range 1:1 and 3.5:1.

9. The method of bleaching kraft pulp without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium and introducing a mixture of chlorine and chlorine dioxide into the aqueous suspension.

10. The method of bleaching kraft pulp without substantial degradation of the fiber which comprises suspending the material to be bleached in an aqueous medium having distributed there-through an alkaline material, and introducing into the aqueous suspension a gaseous mixture containing chlorine and chlorine dioxide.

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