

UNITED STATES PATENT OFFICE

2,235,837

BLEACHING CELLULOSE

John Ogden Logan, Niagara Falls, N. Y., assignor
to The Mathieson Alkali Works, Inc., New York,
N. Y., a corporation of Virginia

No Drawing. Application September 1, 1937,
Serial No. 161,969

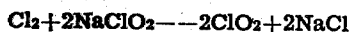
3 Claims. (Cl. 8—108)

It has hitherto been proposed to bleach cellulosic materials with aqueous solutions of chlorites, particularly with acid aqueous solutions of chlorites. Such bleaching processes have the general advantage that, properly applied, the degradation of the cellulosic material normally incident to the use of conventional bleaching agents, chlorine and hypochlorites for example, is avoided. My invention relates to improvements in the bleaching of cellulosic materials with chlorites and chlorine.

In referring to chlorites I refer to the alkali metal and alkaline earth metal salts of chlorous acid, HClO_2 , as distinguished from hypochlorites, salts of hypochlorous acid, HClO , and from chlorates, salts of chloric acid, HClO_3 .

In conventional bleaching of cellulosic material with chlorine or hypochlorites, some degradation of the cellulosic material is usually involved in bleaching to the extent ordinarily required, and extensive degradation in such operations is avoided only by rigorous control. Using chlorites, however, satisfactory bleaching can be effected without such degradation. I do not know what differences in the mechanism of bleaching explain this difference in the action of these bleaching agents upon cellulosic material, but the lack of degradation is generally characteristic of bleaching with chlorites and the appearance of degradation is generally characteristic of bleaching with chlorine or hypochlorites.

I have now discovered that chlorine, introduced into an aqueous solution of a chlorite in contact with cellulosic material to be bleached, instead of acting upon the cellulosic material to bleach it with the accompanying degradation characteristic of chlorine apparently reacts with the chlorite to liberate chlorine dioxide which in turn effects the bleaching of the cellulosic material but without substantial degradation. The reaction apparently involved may be typified as follows:



But whatever the correct explanation may be, I have found that the introduction of chlorine into an aqueous solution of a chlorite in contact with cellulosic material to be bleached effects a bleaching characteristic of chlorites rather than of chlorine. In the process of my present invention several advantages are derived by application of this discovery.

The improved bleaching process of my invention consists essentially of introducing chlorine into an aqueous solution of a chlorite while this

solution, the bleaching bath, is in contact with the cellulosic material to be bleached. This bleaching operation may be carried out as a single operation, or as a series of repeated operations. It may, with particular advantage, be used to complete a bleaching operation initiated by bleaching the cellulosic material to a point short of substantial degradation with chlorine or a hypochlorite. Several important advantages can be obtained by this improved bleaching operation of my invention, both as an operation considered alone and as one step in a combined bleaching operation.

The proportion of chlorine used in conjunction with the chlorite in carrying out my invention should with advantage approximate 25%–30% of the amount corresponding to the available chlorine content of the chlorite used and should not exceed about 50% of this amount. A proportion of 25% of the amount corresponding to the available chlorine content of the chlorite is the proportion indicated by the type reaction cited previously. Frequently, however, a somewhat larger proportion is necessary to effect complete reaction of the chlorite present, and within the limit indicated the use of such an excess does not seriously impair the results obtained.

The bleaching operation of my invention may be carried out over a wide range of temperature and a wide range of alkalinity and acidity. 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 the acidity or alkalinity of the bleaching bath is not usually critical, control of acidity or alkalinity and the addition of reagents to effect such control can be dispensed with in many cases. Similarly, extreme problems of corrosion of equipment used for carrying out the operation can be avoided by avoiding high temperatures and highly acid solutions. The bleaching action of the chlorite as such is increased by an amount corresponding to the amount of chlorine reacting with the chlorite, although this action is characteristic of the chlorite rather than chlorine, thus making possible a saving with respect to the amount of chlorite required. In some instances, properties of the bleached cellulosic material have been improved.

The following examples will illustrate applications of the bleaching process of my invention:

Example I

A kraft pulp with a bleach demand of 12% was chlorinated, in aqueous suspension, with 10% (by weight) of chlorine, this being the maximum proportion of chlorine which could be used without substantial degradation of the pulp. This partially bleached pulp was then resuspended in water, a 5% suspension, containing in solution a proportion of sodium chlorite corresponding to 1.5% (by weight) available chlorine and 0.45% (by weight) of chlorine was introduced into this solution, the rate of chlorine introduction being adjusted so that the total was introduced over about 30 minutes. The bleaching action was permitted to continue for about 90 minutes after the introduction of chlorine had been completed. The temperature of the bleach bath was maintained at about 20° C. and the pH of the bleaching bath was held at about 4.2 by appropriate additions of sodium acetate-acetic acid as buffers.

Example II

A kraft pulp with a bleach demand of 12% was chlorinated, in aqueous suspension, with 10% (by weight) of chlorine, this being the maximum proportion of chlorine which could be used without substantial degradation of the pulp. This partially bleached pulp was then resuspended in water, a 5% suspension, containing in solution a proportion of sodium chlorite corresponding to 1.5% (by weight) available chlorine and a total of 0.36% (by weight) of chlorine was introduced into this solution at intervals while maintaining a temperature of about 40° C. The pH of the bleaching bath, uncontrolled, remained within the range 7.2-8.3.

Example III

A sulfite pulp with a bleached demand of 7% was bleached in successive stages, first in a 3% aqueous suspension containing in solution an amount of sodium chlorite corresponding to a concentration of available chlorine equal to 2.2 g. per liter with introduction of 1.8% of chlorine while maintaining a temperature of 10°-15° C. over a period of 4 hours and 45 minutes and, second, a 13% aqueous suspension containing in solution an amount of sodium chlorite corresponding to 2% available chlorine on the weight of the pulp with introduction of 0.6% of chlorine while maintaining a temperature of 15° C. over a period of 1 hour.

Example IV

A sulfite pulp with a bleach demand of 7% was bleached in successive stages, first in a 3% aqueous suspension to which 4.2% of chlorine was added over a period of 2 hours 10 minutes while maintaining a temperature of 20° C. and second, in a 13% aqueous suspension containing in solution an amount of sodium chlorite corresponding to 2% available chlorine with introduction of 0.6% chlorine while maintaining a temperature of 18°-23° C. for a period of 4 hours and 45 minutes. The pH value of the bleaching bath ranged from 3.8 to 11.5.

The bleaching process of my invention is also useful in the bleaching of other cellulosic materials, such as cotton linters, cotton textiles and rayon. The following examples will illustrate applications of the present invention to such cellulosic materials:

Example V

100 g. of cotton linters were placed in a water

solution containing 3 g. available chlorine in the form of sodium chlorite and adjusted to pH 4. 0.9 g. of chlorine were added as chlorine water bringing the liquid volume to 1.9 l. The mass was heated to 55° C. and maintained at that temperature for 3½ hours from the time heating was started. The linters were then washed.

Example VI

100 g. of cotton linters were placed in a water solution containing 1.5 g. available chlorine in the form of sodium chlorite. 0.45 g. of chlorine was added as chlorine water bringing the liquid volume to 1.9 l. The mass was heated to 40° C. and maintained at this temperature for 3¾ hours. The linters were then washed.

Example VII

25 g. of viscose rayon were placed for ½ hour at room temperature in a solution containing 1.6 g. available chlorine in the form of sodium chlorite to which was added 0.4 g. chlorine as chlorine water. The final volume was 500 cc. The rayon was then washed.

Example VIII

25 g. of viscose rayon were placed for ½ hour at 60° C. in a solution containing 1.6 g. available chlorine in the form of sodium chlorite to which was added .4 g. chlorine as chlorine water. The final volume was 500 cc. The rayon was then washed.

Example IX

1 yard of cotton cloth weighing about 110 g. was immersed in a solution containing 3 g. available chlorine in the form of sodium chlorite to which was added 0.9 g. of chlorine as chlorine water bringing the volume to 1.9 l. The mass was heated to 57° C. and maintained at that temperature for 3½ hours from the time heating was started. The cloth was then washed. The breaking strength of the bleached cloth was 44.8 while that of the unbleached was 48.9.

Example X

1 yard of cotton cloth weighing about 110 g. was immersed in a solution containing 1.5 g. available chlorine in the form of sodium chlorite which had been adjusted to pH 4 before 0.45 g. chlorine were added. The final volume was 1.9 l. The action was allowed to continue for 1½ hours at 38-45° C. after which the cloth was washed. The breaking strength of the bleached cloth was 43.5 while that of the unbleached was 44.6.

In each of the above examples a satisfactory degree of bleaching was attained with substantially no degradation of the cellulosic material.

Chlorine to be introduced into the aqueous solution of a chlorite in contact with a cellulosic material to be bleached, in accordance with my invention, may be introduced as chlorine gas or as chlorine water, although in the latter case due allowance must be made for the increased volume of the bleaching bath incident to such addition of water with the introduced chlorine.

In bleaching with chlorine or with hypochlorites, the bleaching bath will contain hypochlorite ions, the result of dissociation of hypochlorous acid in the first and the result of dissociation of the hypochlorite in the second. I accordingly refer to bleaching baths in which bleaching is effected by chlorine or hypochlorite as aqueous solutions containing the hypochlorite ion. In the combined operation embodying a preliminary bleach with chlorine or hypochlorite,

the preliminary bleach is carried only to a point short of that at which substantial degradation of the cellulosic material would be involved, and is then completed, without degradation of the cellulosic material, by introducing chlorine into an aqueous solution of a chlorite in contact with the thus partially bleached cellulosic material.

I claim:

1. In the bleaching of cellulosic material, the improvement which comprises completing the bleaching by introducing free chlorine into an aqueous solution of a chlorite in contact with the material to be bleached and controlling the proportion of chlorine used in conjunction with the chlorite so as not to exceed approximately 50% of the amount corresponding to the available chlorine content of the chlorite used.

2. In the bleaching of cellulosic material, the improvement which comprises bleaching the material to a point short of substantial degradation

by contact with an aqueous solution containing the hypochlorite ion, thereafter completing the bleaching by introducing free chlorine into an aqueous solution of a chlorite in contact with the material, and controlling the proportion of chlorine used in conjunction with the chlorite so as not to exceed approximately 50% of the amount corresponding to the available chlorine content of the chlorite used.

3. In the bleaching of cellulosic material the improvement which comprises completing the bleaching by introducing gaseous chlorine into an aqueous solution of a chlorite in contact with the material to be bleached, and controlling the proportion of chlorine used in conjunction with the chlorite so as not to exceed approximately 50% of the amount corresponding to the available chlorine content of the chlorite used.

JOHN OGDEN LOGAN. 20