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BLEACHING TREATMENT FOR CELLULOSIC MATERIALS

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This invention relates to the bleaching of cellulosic materials, more particularly wood pulp of either the sulphite or sulphate type.

A primary object of the invention is to produce pulps having physical qualities, including, particularly, good brightness value with substantially no fiber degradation, equivalent or superior to those produced by known bleaching processes with less chemical usage and/or with fewer treatments, rendering the processes of this invention less costly and less complicated.

Bleached cellulosic materials of this invention are prepared by a bleaching sequence which includes as one stage thereof a novel treatment of improved efficiency. This treatment may be included as a final or late stage in any conventional bleaching sequence, and the treatment is so effective with respect to increment in brightness value without material loss in fiber strength that it may be used as a final stage in a sequence involving as few as three stages for the production of sulphate pulps having physical values heretofore obtained only in five or six stage treatments. The cost saving in elimination of even a single stage of a refining sequence is well recognized, since operations of increasing the density and washing intervene between each "stage" of a sequence, as the term "stage" is used in the art. With elimination of a stage, not only is handling eliminated and time saved, but there is also a saving in investment in thickeners and washers.

The treatment of this invention comprises subjecting semi-bleached pulp in a single stage, i. e., without intervening washing, to the action of a chlorite and a hypochlorite under conditions initially favoring action of the hypochlorite on the pulp and subsequently under different conditions favoring action of the chlorite on the pulp.

We have found that savings in chemical usage, as well as stronger pulps without diminished brightness values and more efficient over-all bleaching, may be obtained by subjecting semi-bleached pulp in one stage of a sequence to the action of a mixture of a hypochlorite and a chlorite, and that the conditions of treatment may be so controlled that initial conditions, suitable for optimum bleaching action by the hypochlorite compound of the hypochlorite-chlorite mixture, cause little or no action of the chlorite of the mixture on the pulp and substantially no consumption thereof or change in the bleaching potentialities of the chlorite component. In particular, we have found that initial control of pH to about 9 substantially entirely inhibits the action of the chlorite component of the mixture while favoring action of the hypochlorite component of the mixture.

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Accordingly, after initial conditions favoring the action of the hypochlorite component of the mixture have been maintained for such time as to cause substantially complete consumption of the hypochlorite component, the pH condition is changed to favor action on the pulp by the chlorite component of the mixture until substantially all of the chlorite is consumed. Highly efficient chemical usage with respect to both components is thus attained. The chlorite is activated by the change in pH and its action follows the action of the hypochlorite without intermediate washing. The desirable changed pH is below 5, preferably about 4.

In the case of kraft pulp, highest physical values are attained when the treatment of this invention is preceded by hot (140–210° F.) caustic digestion and preferably by a combination prebleach-chlorination treatment wherein the amount of bleaching reagent added as hypochlorite in the initial bleach is such as to provide a chlorine equivalent input of not more than 50% and not less than 20% of the total chlorine equivalent input of the entire sequence.

Typical treatments of the invention are as follows:

Example I (sulphate)

A softwood kraft pulp was pre-treated with 5.4% chlorine at a stock density of 4% for 1 hour at 65° F., and then was washed.

As a second stage, the pulp was digested with 2.0% NaOH at 14.5% stock density for 1 hour at 175° F., and was then washed.

As a third and final stage, the pulp was suspended in aqueous solution containing a mixture of sodium hypochlorite and sodium chlorite, in a ratio, calculated as equivalent chlorine, of 1.67 to 1.0, the mixture comprising 1.05% chlorine equivalent in the form of sodium hypochlorite and 0.40% sodium chlorite, based upon the bone-dry weight of the pulp, at a stock density of 14.5%, pH of 10–11, and temperature of 100 to 110° F. until the hypochlorite was substantially consumed, i. e., for about two hours, at which time it was ascertained that the chlorite content was substantially unchanged. The stock density was then lowered to 4%, the liquor acidified to bring the pH to about 4 and the temperature increased to 170 to 180° F. and maintained until practically all of the chlorite was consumed or for

about 1 to 2 hours. The pulp was then washed, antichlored, and again washed.

The bleached pulp had the following physical characteristics:

Brightness (G. E. reflectance value)	84.9
Mullen	144
Tear	299
Beater value [2×Mullen (144)+Tear (299)]	587

Example II (sulphate)

Brightness was substantially increased by a pretreatment wherein the first stage comprised a combination treatment, including subjecting the pulp to the action of 8% hypochlorite, based upon the bone-dry weight of the pulp, at 8% stock density and 80° F. for one hour, with subsequent dilution, without intervening washing, to 4% stock density with chlorine water to give 2.7% chlorine, and maintained for one hour at 65° F. The pulp was then washed.

The second stage digestion was carried out with 2% NaOH at 14.5% stock density for one hour at 175° F. and the pulp was then washed. The third stage was identical with Example I, except that the mixture comprised 0.7% chlorine equivalent in the form of sodium hypochlorite and 0.27% sodium chlorite.

This bleached pulp had the following physical characteristics:

Brightness (G. E. reflectance value)	89
Mullen	142
Tear	283
Beater value [2 × Mullen (142) + Tear (283)]	567

Example III (sulphate)

A softwood kraft pulp was given the same treatment as in the first and second stages of Example II.

As a third stage, the pulp was subjected in aqueous solution to the action of a mixture of hypochlorite and chlorite comprising 0.7% chlorine equivalent in the form of sodium hypochlorite and 0.33% sodium chlorite, based on the bone-dry weight of the pulp, at a stock density of 14.5% pH of 10 to 11 and temperature of 140° F. When the hypochlorite was substantially consumed, the stock density was lowered to 13.5% and the pH brought to about 4. The temperature was maintained at about 140° F. until practically all of the chlorite was consumed. The pulp was then washed, antichlored and rewashed.

The bleached pulp had the following physical characteristics:

Brightness	87
Mullen	153
Tear	275
Beater value	581

As shown by the above examples, a pretreatment of kraft stock with a combination prebleach and chlorination, as distinguished from mere chlorination as in Example I, increases the brightness value, particularly where, as in the case of Examples II and III, the amount of equivalent chlorine input in the initial hypochlorite treatment is from 20 to 50% (actually about 42% in Examples II and III) of the total equivalent chlorine input of the entire sequence.

Example IV (sulphite)

A normal softwood sulphite raw stock made by cooking spruce wood with a calcium-bisulphite

acid comprising 5% free SO_2 and 1% combined SO_2 in the normal way was treated with 5½% chlorine at prevailing water temperature and at 4% stock density for 15 minutes, then washed, then treated with 1% caustic soda at 4% stock density at prevailing water temperature for about five minutes, and thickened.

A portion of the pulp was then bleached with 1.93% chlorine in the form of soda-bleach plus ¾% caustic soda at 10% stock density and 110° F. for four hours to form a control. The bleached pulp was then washed, antichlored and again washed.

A second portion of the semi-bleached (i. e., prechlorinated, washed, caustic-soaked, thickened) softwood sulphite pulp was suspended in aqueous solution containing a mixture of hypochlorite and chlorite, in a ratio, calculated as equivalent chlorine, of 1.5 to 1.8, the mixture containing 1.05% chlorine equivalent in the form of sodium hypochlorite plus 0.41% sodium chlorite plus 0.3% caustic soda, based on the bone-dry weight of the pulp. It was left at a stock density of 10% and temperature of 110° F. until the hypochlorite was substantially consumed, i. e., for about two hours, at which time it was ascertained that the hypochlorite had been substantially consumed but that the chlorite content was substantially unchanged. The stock density was then lowered to 4%, the suspension acidified to bring the pH to about 4 and the temperature increased to 180° F. and maintained until practically all the chlorite was consumed, or for about two hours. The pulp was then washed, antichlored, and again washed.

The two bleached sulphite pulps had the following physical characteristics:

	Control (alkaline bleach)	Hypochlorite-Chlorite Bleach
Brightness	88.6	89.6
Mullen	112	118
Tear	177	185
Beater value	401	421

Stock density favoring the hypochlorite action may be from 10 to 15%, stock density favoring the chlorite action may be from 3 to 14%. Temperatures favoring hypochlorite action range from 90 to 150° F. and chlorite action from 140 to 190° F.

The chlorine equivalent ratio of hypochlorite to chlorite in the mixture should not be more than 1.8 to 1.0 for the production of products having the characteristics of the examples, and preferably should be between 1.5 and 1.8 to 1.0.

The term hypochlorite is used with the intention that it include the alkaline hypochlorites commonly used for bleaching purposes, and the term chlorite those alkali metal and alkaline earth metal chlorites which have been found serviceable as bleaching agents as described in Mathieson Alkali Works Patents Nos. 2,100,496 and 2,145,062 and elsewhere in the literature.

We claim:

1. Method of bleaching a cellulosic material comprising subjecting the material to the action of an aqueous solution of hypochlorite and chlorite maintained first at a pH above 9, consumption of any substantial amount of chlorite being thereby avoided, and then at a pH below 5, the solution being brought to the lower pH upon substantial exhaustion of the hypochlorite, the chlorite being the effective bleaching reagent thereafter.

2. The method of claim 1 as applied to the bleaching of wood pulp.

3. The method of claim 1 where the cellulosic material is sulphate pulp and the defined procedure is preceded by treatment of the pulp with hypochlorite and chlorine, the input of hypochlorite on the basis of equivalent chlorine being not less than 20% nor more than 50% of the total equivalent chlorine input of the entire sequence.

4. In the bleaching of wood pulp the improvement which resides in treating the pulp with an aqueous solution of hypochlorite and chlorite in which the ratio of hypochlorite to chlorite on the basis of equivalent chlorine lies initially within the range 1.5 to 1.8, the solution being maintained first at a pH above 9 and a temperature between 90° and 150° F. and then at a pH below 5 and a temperature between 140° and 190° F., the solution being brought to the lower pH following exhaustion of the hypochlorite, the chlorite being the effective bleaching reagent thereafter.

5. A process according to claim 4 further characterized in that the pulp is treated in an amount providing a stock density during the treatment at the higher pH of from 10 to 15% and in that the stock density upon exhaustion of the hypochlorite is reduced to a point within the range 3 to 14%.

6. The improvement of claim 4 where the pulp is sulphate pulp which has been previously treated sequentially with hypochlorite and chlorine, the input of hypochlorite on the basis of equivalent chlorine being not less than 20% nor more than 50% of the total equivalent chlorine input of the entire process.

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