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BLEACHING OF CELLULOSIC MATERIALS WITH CHLORINE DIOXIDE

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ABSTRACT OF THE DISCLOSURE

There is provided a novel process of bleaching woodpulp to a high degree of brightness and color stability wherein the strength of the bleached pulp is substantially the same as that of unbleached pulp. In said process unbleached woodpulp is bleached with a mixture of chlorine and chlorine dioxide, treated with alkali, and then treated with chlorine dioxide.

This case is a continuation-in-part of S.N. 378,417, filed June 26, 1964 and now abandoned.

This invention relates to an improved method of bleaching cellulosic materials. More particularly, it relates to a method of bleaching woodpulp to high brightness and good color stability without significant loss of strength.

In making chemical woodpulps, such as those obtained by sulfite, soda and kraft processes, bleaching has been effected by multi-stage processes which may begin with treatment of the unbleached pulp in water with chlorine. Although subsequent stages of the multi-stage process may carry out bleaching without significant damage to pulp strength (often measured by pulp viscosity) or loss of color stability, the chlorination often decreases pulp strength and makes the pulp susceptible to undesirable yellowing with age.

When chlorine dioxide is used in replacement of chlorine in the chlorination stage of a multi-stage kraft pulp bleaching process, the loss in strength characteristic of chlorine treatment is avoided and color stability is improved, but the brightness obtained after three or more stages of bleaching is even lower than that obtained when chlorine is used in the first stage.

It has been proposed to bleach woodpulp in aqueous medium with a mixture of chlorine and chlorine dioxide but the bleached woodpulp so made did not possess the desired brightness and color stability which are obtainable by the present method. Reference is made to U.S. Pat. No. 2,166,330 and Canadian Patent No. 552,007.

It is an object of the present invention to provide a method for bleaching cellulosic materials by which there are obtained improved brightness, color stability and pulp strength characteristics. A further object is to bleach woodpulp to a brightness greater than that produced by prior methods and to produce a pulp of good color stability and of a strength substantially that of the unbleached fibers. Other objects and advantages will be apparent from a reading of this specification.

In accordance with this invention, unbleached woodpulp is bleached with a mixture of chlorine and chlorine dioxide, followed by subsequent treatments with alkali and chlorine dioxide. The important benefits attending the use of a mixture of chlorine and chlorine dioxide are realized fully only after the subsequent treatment with chlorine dioxide. Thus, not only is the brightness greater after the chlorine dioxide treatment step but brightness after heating at 105 degrees centigrade is also better,

indicating improved resistance to yellowing when in the described plural and multi-stage processes the first bleaching is effected by a mixture of chlorine and chlorine dioxide. This is noteworthy because it might have been expected that subjection of the bleached pulps to additional bleaching stages with additional oxidizing agents would eliminate the higher brightnesses obtained from the first stage treatment. The higher brightnesses and color stabilities are still apparent even when other bleaching stages are employed after alkali extraction and before chlorine dioxide treatment or after chlorine dioxide treatment.

In practicing the invention, woodpulp of a consistency between about two and twelve percent (weight of dry pulp in 100 pounds of a mixture of dry pulp and water) is first bleached with a sufficient amount of mixed chlorine and chlorine dioxide to provide the oxidizing power, expressed in terms of available chlorine, for bleaching the color bodies associated with the pulp. The quantity of available chlorine used is dependent on the kind of pulp and may be ascertained by known techniques. One pound of chlorine is equivalent to one pound of available chlorine and one pound of chlorine dioxide is equivalent to 2.63 pounds of available chlorine. Although chlorine dioxide and chlorine may be employed in such a ratio that each furnishes about half of the available chlorine provided the mixture, it is preferred that from about 20 to about 95 percent (by weight) of the available chlorine provided by the mixture be furnished by the chlorine dioxide, and it is even more preferred that from about 40 to about 95 percent (by weight) of said available chlorine be furnished by the chlorine dioxide. The temperature of the first stage bleaching is from 0 to 35 degrees centigrade and the bleaching takes from about 5 to 60 minutes. Although various amounts of available chlorine may be employed to bleach out the color bodies present, at a three percent consistency the available chlorine used may be 3 to 10 percent (3 to 10 pounds of available chlorine per 100 pounds of dry pulp).

After treatment with the mixture of chlorine and chlorine dioxide and pulp is of 3 to 18 percent consistency. It is then subjected to alkali extraction with a caustic alkali, e.g., sodium hydroxide, usually to the extent of 0.25 to 5 percent, based on the weight of the dry pulp. The extraction temperature is from 40 to 130 degrees centigrade and the extraction takes from 5 to 180 minutes.

After extraction, the pulp is treated with chlorine dioxide. At this stage the pulp is of a consistency of from about five to fifteen percent and the amount of chlorine dioxide employed is from about 0.1 to 2 percent of the pulp. The chlorine dioxide treatment is usually undertaken at a temperature from 30 to 90 degrees centigrade and lasts for from 5 to 300 minutes.

As was previously mentioned, the pulp may be subjected to other bleachings, in addition to the treatments with mixture of chlorine and chlorine dioxide, hot alkali extraction and chlorine dioxide mentioned. For example, after hot alkali extraction and before chlorine dioxide bleaching the pulp may be treated with hypochlorite or hypochlorite followed by peroxide. Various suitable hypochlorites may be used, those of the alkali and alkaline earth metals, such as sodium and calcium hypochlorites being preferred. At this stage the woodpulp is of a consistency of five to fifteen percent and the hypochlorite bleaching is carried out at a temperature of about 20 to 70 degrees centigrade for about 5 to 180 minutes, sufficient hypochlorite being utilized to provide from about 0.1 to 4 percent available chlorine based on the weight of the pulp. The subsequent treatment with peroxide, if employed, utilizes from 0.05 to 4 percent of hydrogen peroxide, based on the weight of the pulp. The pulp treated is at a consistency of 5 to 35 percent and is treated for

5 to 300 minutes at a temperature of about 3 to 90 degrees centigrade.

In addition to the processes mentioned supra, many other variations of the invented process may be used, providing that the first step is a bleaching of woodpulp with a mixture of chlorine and chlorine dioxide, as described, followed at some suitable point in the overall bleaching process by alkali and chlorine dioxide treatments. Thus, additional bleachings with chlorine dioxide may be effected and additional extractions with alkali may be advantageous.

The following examples are given to illustrate the invention and to assist in the ready understanding thereof. All parts are by weight and all temperatures are in degrees centigrade, unless otherwise indicated.

EXAMPLE 1

Samples of unbleached Spruce sulfite pulp were mixed with varying ratios of chlorine and chlorine dioxide as shown in Table 1, to provide a total weight of chlorine and chlorine dioxide equivalent to 5 pounds of available chlorine per 100 pounds of pulp at 3 percent consistency, maintained for one hour at 25 degrees centigrade and then washed with fresh water.

Each sample of pulp was then treated with 2 percent NaOH based on the dry weight of the pulp, at 15 percent consistency, at 60 degrees centigrade for two hours and washed with water.

Following caustic extraction, each sample was treated with 0.5 percent chlorine dioxide based on dry pulp, at 6 percent consistency, at 70 degrees centigrade for three hours and washed with water. In this treatment and in those described in the other examples and in this specification, it is seen that the pulp is usually preferably washed with water after the various treatment stages. Such washings are effected to remove substantially all the excess chemicals of the previous treatment.

The brightness of the samples (expressed in terms of the General Electric Brightness Standard) was determined before and after heating in an oven at 105 degrees centigrade for 18 hours to simulate ageing. The results are shown in Table I.

TABLE I.—TREATMENTS OF SPRUCE SULFITE PULP OF EXAMPLE 1

Percent available chlorine by weight in the mixture of chlorine and chlorine dioxide	G.E. brightness, percent		Viscosity centipoises
	Before ageing	After ageing	
0	87.0	78.7	34.4
22.6	87.4	79.6	36.0
39.7	88.1	80.2	35.1
53.0	88.8	80.8	30.9
63.7	88.8	80.8	33.6
72.0	89.1	79.8	33.0
79.7	89.0	79.7	31.9
86.0	88.6	79.6	32.2
91.3	88.5	78.9	33.2
95.9	88.2	78.5	32.2
100	86.9	77.5	24.1

EXAMPLE 2

Samples of unbleached Southern Pine Kraft pulp were treated with varying ratios of chlorine and chlorine dioxide to provide a total weight of chlorine and chlorine dioxide equivalent to 6.2 percent available chlorine, at 3 percent consistency, at 25 degrees centigrade for one hour and then washed with water.

The second stage of treatment for all samples was with 2 percent NaOH on a dry pulp basis, at 15 percent consistency, and 60 degrees centigrade for two hours.

After washing, each sample was treated with one percent ClO_2 based on dry pulp, at 6 percent consistency, at 70 degrees centigrade for three hours and was washed again. The results are shown in Table II.

TABLE II.—TREATMENTS OF SOUTHERN PINE KRAFT PULP OF EXAMPLE 2

Percent available chlorine by weight in the mixture of chlorine and chlorine dioxide	G.E. brightness, percent		Viscosity, centipoises
	Before ageing	After ageing	
0	77.3	73.7	10.0
22.6	77.9	74.2	10.3
39.7	79.6	75.9	10.0
53.0	80.2	76.6	10.0
63.7	80.8	77.3	10.1
72.0	81.2	77.5	10.0
79.7	81.3	77.4	9.9
86.0	82.0	77.8	10.2
91.3	81.8	77.3	10.0
95.9	81.1	76.7	10.4
100	79.7	75.0	8.7

EXAMPLE 3

Some of the samples of unbleached Southern Pine Kraft pulp of Example 2 after the first three stages, treatment with mixed chlorine and chlorine dioxide, caustic extraction and chlorine dioxide treatment were subjected to two additional bleaching stages, namely, a second caustic extraction under identical conditions to those used in the first caustic extraction and to a second chlorine dioxide treatment under identical conditions except that only 0.5 percent ClO_2 based on the dry weight of the pulp was used.

The results are shown in Table III.

TABLE III.—TREATMENTS OF SOUTHERN PINE KRAFT PULP OF EXAMPLE 3

Percent available chlorine by weight in the mixture of chlorine and chlorine dioxide	G.E. brightness, percent		Viscosity, centipoises
	Before ageing	After ageing	
0	88.7	85.3	9.2
22.6	88.7	85.3	9.5
39.7	89.0	85.7	9.4
53.0	89.5	86.5	9.3
63.7	90.0	87.5	9.4
72.0	90.7	87.4	9.2
79.7	90.4	87.4	8.9
86.0	90.6	87.2	9.1
91.3	90.7	87.1	9.4
95.9	89.9	86.5	9.4
100	89.5	85.6	8.1

EXAMPLE 4

An unbleached kraft pulp made from a mixture of softwoods native to central British Columbia was treated in three ways with total weights of chlorine and chlorine dioxide equivalent to 7 percent available chlorine based on the weight of the pulp, 100 percent chlorine, 63.7% chlorine and 36.3% chlorine dioxide by weight of the mixture and 100 percent chloride dioxide being used. In each case, the treatment was carried out at 3 percent consistency at 25 degrees centigrade for one hour. After washing, the bleaching was followed by hot caustic extraction with 2.5 percent NaOH based on the weight of the pulp, at 15 percent consistency, and 60 degrees centigrade for two hours and another washing.

A variety of subsequent bleaching stages was carried out, each including at least one chlorine dioxide stage, to give the sequences:

CED
CEHD
CEHDP
$CE_1HD_1E_2D_2$
$CE_1D_1E_2D_2$

wherein:

C=treatment with mixed chlorine and chlorine dioxide;
E=caustic extraction;
H=hypochlorite;
P=peroxide; and
D=chlorine dioxide.

The conditions for the later stages were:

H=1 percent available chlorine as hypochlorite based on the weight of pulp, 6 percent consistency, 40 degrees centrigrade, 3 hours, and pH 10;

P=0.38 percent H_2O_2 based on the weight of pulp, 6 percent consistency, 70 degrees centrigrade, 3 hours, buffered at a pH of 10.5;

E=2.0 percent NaOH based on the weight of pulp, 15 percent consistency, 60 degrees centrigrade, 3 hours; and

D=various percentages of ClO_2 based on the weight of pulp as shown in Table IV as subscripts, 6 percent consistency, 70 degrees centrigrade, 3 hours.

TABLE IV

Unbleached Kraft Pulp of Example 4

Sequence	Composition of chlorination chemicals	G.E. brightness, percent: Before ageing	G.E. brightness, percent: After ageing	Viscosity centipoises
$CED_{1.2}$	100% chlorine	80.2	72.5	25.7
	63.7% chlorine+36,3% chlorine dioxide	84.9	78.2	31.7
	100% chlorine dioxide	80.1	74.2	37.2
$CEHD_{0.82}$	100% chlorine	86.7	77.1	23.7
	63.7% chlorine+36.3% chlorine dioxide	88.7	81.1	28.1
	100% chlorine dioxide	84.2	77.1	33.4
$CEHD_{0.82}P$	100% chlorine	89.9	83.2	21.6
	63.7% chlorine+36.3% chlorine dioxide	90.4	85.1	24.9
	100% chlorine dioxide	88.2	83.7	31.0
$CED_{1.2}ED_{0.3}$	100% chlorine	92.2	84.7	21.9
	63.7% chlorine+36,3% chlorine dioxide	92.7	87.3	28.5
	100% chlorine dioxide	90.8	85.9	32.3
$CEHD_{0.82}ED_{0.3}$	100% chlorine	92.2	84.8	19.6
	63.7% chlorine+36.3%chlorine dioxide	92.4	86.5	22.1
	100% chlorine dioxide	90.6	86.6	26.6

Whereas in the previously disclosed methods of using mixtures of chlorine and chlorine dioxide and the brightness disclosed was about 70 to 75 percent before ageing, the present invention produces sulfite woodpulp of 88 to 89 percent brightness, as shown in Example 1 and kraft woodpulp of brightness of 82 to 85 percent as shown in Examples 2, 3 and 4 in only three stages.

As long as the mixture of chlorine and chlorine dioxide is used in the first step, and a caustic extraction and a chlorine dioxide treatment are included in this order in the subsequent steps, higher brightness both before and after ageing is obtained even when other bleaching stages are included in the sequence, as shown in Example 4. As more bleaching stages and more total bleaching chemical are used, the brightness before and after ageing is higher, but the advantage of using the mixture of chlorine and chlorine dioxide in the first stage, followed by a caustic extraction, and a chlorine dioxide stage is still manifest.

Referring to the pulp viscosities which are an indication of the amount of degradation of the woodpulp fibers, in all cases the pulp viscosity is higher, the more chlorine dioxide and the less chlorine are used in the chlorination stage of the process of this invention. However, use of chlorine dioxide only in the chlorination stage produces a pulp of lower brightness. Therefore, higher brightness and better color stability of the pulp is obtained with a mixture of chlorine and chlorine dioxide in the chlorination stage of the process of this invention while still retaining more of the inherent pulp strength than is obtained with chlorine alone.

Thus, the method of this invention bleaches different types of wood pulp to higher brightness with better color stability than may be obtained with the methods now in use, with the additional advantage that the amount of degradation of the wood pulp fibers is very low.

While there have been described various embodiments of the invention, the composition and methods described are not intended to be understood as limiting the scope of the invention. It is realized that changes therein are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner. It is intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A multistage process for bleaching woodpulp in aqueous medium, said woodpulp having a consistency of from about 2 to about 12 percent, comprising the steps of:

(a) bleaching the woodpulp in a first stage for from about 5 to about 60 minutes at a temperature from about 0 to about 35 degrees centigrade, with a mixture of chlorine and chlorine dioxide in which from about 20 to about 95 percent by weight of the available chlorine is furnished by the chlorine dioxide; and

(b) subjecting the woodpulp in a second stage to extraction with from about 0.25 to about 5 percent caustic alkali based upon dry pulp weight at a temperature from about 40 to about 130 degrees centigrade for from about 5 to about 180 minutes; and

(c) in a subsequent chlorine dioxide stage, treating the woodpulp with from about 0.1 to about 2 percent chlorine dioxide by weight of pulp at a temperature from about 30 to about 90 degrees centigrade for from about 5 to about 300 minutes.

2. The process of claim 1 in which said woodpulp is washed with water after each stage to remove excess chemicals.

3. The process of claim 1 in which from about 40 to about 95 percent by weight of the available chlorine in said mixture of chlorine and chlorine dioxide is furnished by chlorine dioxide.

4. The process of claim 1 in which said chlorine dioxide treatment stage is applied after a cuastic extraction stage.

5. The process of claim 1 in which said extraction with caustic alkali and said treatment with chlorine dioxide, respectively, are serially applied as the second and third, and fourth and fifth stages of said multi-stage bleaching process.

6. The process of claim 1 wherein the woodpulp is bleached with hypochlorite providing from about 0.1 to about 4 percent of available chlorine by weight of pulp at a temperature of from about 20 to about 70 degrees centigrade for from about 5 to about 180 minutes in the third stage of said multi-stage bleaching process, and said chlorine dioxide bleach is applied in the fourth stage.

7. The process of claim 6 in which said woodpulp is bleached with from about 0.05 to about 4 percent peroxide at a temperature of from about 3 to about 90 degrees centigrade for from about 5 to about 300 minutes after said chlorine dioxide bleach stage.

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