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DELIGNIFICATION AND BLEACHING OF CHEMICAL AND SEMICHEMICAL CELLULOSE PULPS WITH OXYGEN AND CATALYST

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ABSTRACT OF THE DISCLOSURE

Delignification and bleaching of chemical and semichemical cellulose pulps under the action of oxygen in an alkaline medium comprising the treatment of the pulp in the presence of a catalyst, used at a concentration from 0.5 to about 3% by weight on the pulp, selected from the group consisting of barium carbonate, calcium carbonate, magnesium carbonate, zinc carbonate, alkali metal borates and titanium dioxide.

This invention relates to the delignification and bleaching of chemical and semichemical cellulose pulps by the action of oxygen in an alkaline medium.

The bleaching of chemical cellulose pulps for the production of paper or of dissolving pulps for chemical uses generally requires several successive treatments to reach the desired amount of residual lignin and the required brightness.

Bleaching agents commonly used for the treatment of cellulose pulps include chlorine, caustic soda, calcium and sodium hypochlorites, chlorine dioxide, sodium dioxide, hydrogen peroxide; the first are almost exclusively used for delingnification.

The brightening and delignifying action of air or oxygen on cellulose pulps in an alkaline medium has long been known; among the latest publications on the matter are the work of Nikitine and Akim (Proc. Leningrad Acad. of Forestry 75/1956–77/1958–85/1960 and Bum. Prom. 12/1960), U.S. Patent No. 3,024,158, filed on July 2, 1958, by the Kimberley-Clark Corporation, and French Patent No. 1,310,248, filed on March 6, 1961, by Champion Papers.

When operating at a temperature near 100° C. and under partial pressures of oxygen between 5 and 10 bars, the delignifying and bleaching effects are even more marked. However, the elimination of lignin and the material increase in brightness are nearly always accompanied by a significant lowering of the physical characteristics of the cellulose pulps, which makes the method difficult to use commercially.

According to the invention, a method has been discovered which makes it possible, in a multistage bleaching operation, to substitute one operation for the first two operations of chlorination and alkaline extraction, and possibly for a subsequent hypochlorite treatment, the delignification and increase in brightness being usually greater than by known methods.

The method of the invention has the greater advantage of well preserving the physical and mechanical characteristics of cellulose pulps, and even of improving them in some cases, while giving a very complete delignification and a significant increase in brightness.

This method for the delignification and bleaching of chemical and semichemical cellulose pulps under the action of oxygen in an alkaline medium is characterized in that the treatment of the pulps is effected in the presence of a catalyst selected from the group consisting of barium carbonate, calcium carbonate, magnesium carbonate, zinc carbonate, alkali metal borates and titanium dioxide, used at a concentration from 0.5 to about 3% by weight of the pulp.

Magnesium carbonate is the preferred catalyst according to the invention. When used in amounts of about 1% by weight of the pulp, it gives the best results.

According to a preferred embodiment of the invention, the unbleached pulp is treated, in an electrically heated, rotary autoclave, with a solution of caustic soda in the presence of the catalyst, at elevated temperatures, preferably between 90° C. and 130° C., and particularly between 90° C. and 100° C. Oxygen is introduced into the autoclave so as to get the desired pressure, usually in the range 5–10 bars. Once the reaction is over, the autoclave having been degassed and the pulp discharged, the latter is carefully washed and may be subjected to the action of other bleaching agents, such as hypochlorite, peroxides, etc.

The cellulose pulps treated usually have a concentration ranging from 6% to 10%, and 8% to 12% NaOH is preferably used based on the pulp, according to the quality and degree of lignification of the latter.

The concentrations given are concentrations by weight.

The time of reaction at top temperature ranges from half an hour to a few hours, preferably between one and three hours.

The following examples are illustrative of the invention, but are not intended to limit the scope of the same.

EXAMPLE I

Softwood kraft pulp, permanganate number 22.5 (Afnor standard):

Pulp concentration: 6.6%;
Caustic soda concentration based on the pulp: 11.25%;
Operating temperature: 100° C.;
Oxygen pressure at 100° C.: 5.75 bars;
Catalyst: $MgCO_3$ (1% based on the pulp);
Time of treatment: 2 hrs. at 100° C.

The results of the brightness tests and the physical and mechanical characteristics of the untreated unbleached pulp, of the pulp treated in an alkaline medium without a catalyst, and of the pulp treated in the presence of the catalyst, are summarized in the following table:

	Untreated, unbleached pulp	Pulp treated without catalyst	Pulp treated with catalyst
Canadian freeness, cc.	387	425	457
Photovolt brightness (unbeaten pulp)	32	49	52
Yield of pulp after treatment, percent		91.0	92.6
Breaking length, metres	11,350	6,260	9,760
Double folds under 885 g.	2,390	30	1,850
Burst factor	79.2	37	66
Tear factor 100	126	53	90
Permanganate number (Afnor)	22.5	7.3	7.2
Pentosans, Percent (Afnor)	10.6	9.6	9.8
Lignin, percent (No. 11)	4.6	0.7	0.7
Oxygen consumed based on the pulp, percent		ca. 2	ca. 2

A study of the above results evidences the marked effect of the catalyst on the preservation of the breaking length, folding strength, bursting strength and tearing strength.

EXAMPLE II

Maritime pine kraft pulp, permanganate No. 38 (Afnor);
Pulp concentration: 6.6%;
Caustic soda concentration based on the pulp: 10%;
Operating temperature: 100° C.;
Oxygen pressure at 100° C.: 6.8 bars;
Catalyst: $MgCO_3$ (1% based on the pulp);
Time of treatment: 2 hrs. at 100° C.

	Untreated, unbleached pulp	Pulp treated without catalyst	Pulp treated with catalyst
Canadian freeness, cc	369	363	375
Photovolt brightness (unbeaten pulp)	23.5	42	28.5
Yield of pulp after treatment, percent		82	83
Breaking length, metres	7,300	6,970	8,400
Double folds under 885 g	440	480	980
Burst factor	46	48.5	56
Tear factor 100	100.8	85.2	116
Permanganate number (Afnor)	38	12.2	12
Caustic consumed based on the pulp, percent		8.5	9

In the case of this very hard kraft pulp, it may be noticed that the treatment according to the method of the invention makes it possible to obtain a very complete delignification and to improve all the physical characteristics of the treated pulp above those of the initial unbleached pulp.

EXAMPLE III

Hardwood neutral sulphite (Na_2SO_3) pulp (90% poplar, 10% beech):
Concentration of the pulp: 6.6%;
Concentration of NaOH based on the pulp: 10%;
Operating temperature: 100° C.;
Oxygen pressure at 100° C.: 6.8 bars;
Catalyst: 1% $MgCO_3$ based on the pulp;
Time of treatment: 2 hrs. at 100° C.

	Untreated, unbleached pulp	Pulp treated without catalyst	Pulp treated with catalyst
Canadian freeness, cc	394	381	400
Photovolt brightness (unbeaten pulp)	57.5	65	66.5
Yield of pulp after treatment, percent		86.5	87
Breaking length, metres	8,380	5,790	7,620
Burst factor	52.5	28	45.5
Double folds under 885 g	220	8	200
Tear factor 100	85	64	93

The comparative results summarized in the above table evidence the very marked influence of the catalyst. While the pulp delignified with oxygen without the catalyst shows greatly impaired characteristics compared with the initial pulp, the pulp treated in the presence of the catalyst shows characteristics which are but slightly different from those of the initial pulp.

EXAMPLE IV

Softwood unbleached kraft pulp:
Pulp concentration: 6.6%;
Concentration of NaOH based on the pulp: 11.3%;
Oxygen pressure at 100° C.: 4.5 bars;
1% catalyst by weight based on the pulp;
Time of treatment: 2 hrs. at 100° C.

The various catalysts used in these trials are barium and calcium carbonates, titanium dioxide and sodium tetraborate.

	Pulp treated without catalyst	Pulp treated with $BaCO_3$	Pulp treated with $CaCO_3$	Pulp treated with, TiO_2	Pulp treated with $Na_2B_4O_7$
Canadian freeness, cc	394	394	419	369	412
Brightness (unbeaten pulp)	52	50	52	51	52
Breaking length, metres	8,060	9,679	10,500	9,212	9,492
Double folds under 885 g	1,544	1,849	2,296	1,023	1,760
Burst factor	65	72	73	62	72
Tear factor 100	94.7	91.5	95.6	82	89.7

The comparative results summarized in the above table evidence the influence of the catalysts herein described.

The examples illustrating the invention show the advantages of the use of a catalyst in the bleaching of pulps with oxygen in an alkaline medium, which makes it possible to obtain a very complete delignification and a significant increase in brightness, while preserving the physical characteristics of the treated pulps. The commercial application of the method can therefore be contemplated, so as to substitute an oxygen-caustic treatment for the chlorination and alkaline extraction phases at least.

What we claim is:

1. A method for the delignification and bleaching of chemical and semichemical cellulose pulps under the action of oxygen in an alkaline medium, wherein the delignification and bleaching of the pulp is effected with a catalyst, used at a concentration from 0.5 to about 3% by weight of the pulp, selected from the group consisting of barium carbonate, calcium carbonate, magnesium carbonate, zinc carbonate, alkali metal borates and titanium dioxide.

2. A method for the dilignification and bleaching according to claim 1 wherein the catalyst is magnesium carbonate used at a concentration of about 1% by weight of the pulp.

3. A method for the delignification and bleaching according to claim 1 wherein the treatment is effected at temperatures in the range from 90 to about 130° C.

4. A method for the delignification and bleaching according to claim 1, wherein the time of the treatment, at working temperature, is from half an hour to three hours.

5. A method for delignification and bleaching according to claim 1 wherein the oxygen is present at a pressure in the range of 5–10 bars.

6. A method for the delignification and bleaching of chemical and semichemical pulps which comprises delignifying and bleaching the pulp in an alkaline medium and including oxygen and a catalyst selected from the group consisting of barium carbonate, calcium carbonate, magnesium carbonate, zinc carbonate, alkali metal borates and titanium dioxide, said catalyst being in a concentration of from 0.5 to about 3% by weight of the pulp, said delignifying and bleaching being effected at temperatures in the range of from 90 to about 130° C. for a time of from half an hour to a few hours, the oxygen being present at a pressure in the range of 5–10 bars.

7. A method in accordance with claim 6 wherein said pulp has a concentration of from 6% to 10% and the alkali concentration is 8% to 12% based on the pulp.

8. A method for the delignification and bleaching of chemical and semichemical pulps which comprises delignifying and bleaching the pulp in an alkaline medium and including oxygen and a catalyst consisting of magnesium carbonate, said catalyst being in a concentration of from 0.5 to about 3% by weight of the pulp, said delignifying and bleaching being effected at temperatures in the range of from 90 to about 130° C. for a time of from half an hour to a few hours, the oxygen being present at a pressure in the range of 5–10 bars.

9. A method in accordance with claim 8, wherein said pulp has a concentration of 6 to 10% and the alkali concentration is 8 to 12% based on the pulp.

10. A method in accordance with claim 8, wherein the magnesium carbonate is in a concentration of about 1% by weight of pulp.

11. A method in accordance with claim 10, wherein said pulp has a concentration of from 6 to 10% and the alkali concentration is 8 to 12% based on the pulp.

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