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(54) Alkaline-peroxide-oxygen treatment for unbleached and chlorinated chemical pulps.

(57) There are provided improvements relating to the delignification and/or the bleaching of a chemical pulp wherein the cellulosic material is simultaneously treated with an alkali compound, a peroxygen compound and an oxygen gas at partial pressure in the presence of a viscosity protecting catalyst.

FIELD OF THE INVENTION

The present invention relates to the treatment of a cellulosic material and more particularly, relates to improvements in the delignification and/or bleaching of chemical pulps.

BACKGROUND OF THE INVENTION

Bleaching is a continuation of the cooking process in which the lignious material and colouring matter remaining in the chemical pulp are removed selectively with as little degradation of pulp fibre as possible. Bleaching of pulp has advanced to a high degree of sophistication involving multistage procedures. The bleaching of a chemical pulp is accomplished in several stages which together, constitute a bleaching sequence.

Each stage consists of a phase starting with the addition and reaction of a chemical with a pulp, and ending with the washing of the pulp. Within each stage there are many process variables which are dictated by the type of reaction desired in that particular stage and the operating conditions of that stage. These variables include: percent of chemical added and consumed, chemical concentration, consistency, temperature, time and pH.

The delignifying and brightening action of air or oxygen on a chemical cellulosic pulp in an alkaline medium has long been known. The pre-dominant processes are presently carried out at high consistency (25-30%) on pulp previously impregnated with an alkali (usually 2.0 -3.0% NaOH on pulp, oven-dry basis) and a magnesium ion complex - (0.05-0.1% magnesium ion on pulp, oven-dry basis). The pulp is then fluffed and exposed to oxygen at a pressure of 0.6-0.8 MPa at 80-165°C for a reaction time of up to 30 minutes. Developments in oxygen delignification at low (4-5%) and medium - (10-15%) consistencies have been reported and are of interest because they avoid the pressing step necessary to obtain the higher consistencies of 25-30%. The pulp is subjected to an oxygen pressure of 0.5-1.4 MPa at temperatures of from 80-165°C for a reaction time of up to 6 hours. Commonly, these oxygen treatments replace one-half of the chlorine required in normal chlorination stage, dropping the Kappa number from the original value of from 30-35 to about 15-17 on a softwood pulp and from 12-18 to 6-9 on a hardwood pulp. These delignification procedures are accompanied by a decrease in pulp viscosity (by about 30-40%). The processes described above require the use of a highly pressurized vessel to equalize the 0.6-0.8 MPa of oxygen pressure which is required for the delignification stage.

In 1970, oxygen became recognized as being useful in a conventional caustic extraction stage. Thus, a small amount of oxygen in the extraction stage, herein called an oxidative extraction stage, made it possible to decrease the Kappa number and hence the chlorine dioxide or hypochlorite requirements in later stages. This development was sufficiently attractive to prompt a rapid acceptance of the oxidative extraction stage on a commercial scale, and especially since its implementation was fairly straightforward. If a mill had an upflow extraction tower available to provide some pressurization in the form of a hydrostatic head, then the only modification required to an existing bleach plant was the installation of an in-line static mixer or a high-shear type mixer. If a mill had a downflow tower, the desired effect could be obtained by installing a high-shear type mixer followed by an upflow pre-retention tube leading to the top of the tower. Conditions to carry out an oxidative extraction step are as follows: pulp consistency 9-14%, temperature 50-80°C, retention time 3-60 minutes, NaOH charge 2-4% on pulp OD basis, pressure of oxygen at least 0.14 MPa.

Kruger and Suss, in 1982 International Sulfite Pulping Conference, page 143-148 Tappi Proceedings, teach that an oxygen and peroxide treatment of a softwood sulphite pulp can give a 2-point brightness increase compared to peroxide alone. In their process, they teach that the oxygen pressure must be 0.3 MPa, and that silicate stabilization of peroxide is necessary. Also they teach an OP treatment of a sulphite pulp which is not further treated with other bleaching stages. Recently Kruger and Suss have published a paper referring to an alkaline peroxide oxidative extraction on sulphite pulps only after treatment with an acidic nitrogen - (i.e., N-EOP), Das Papier, 38, Jahrgang Heft 11, 1984, pages 529-534.

It is also known from U.S. Patent 4,459,174 to Papageorges et al to utilize a sequential sequence which comprises an oxygen treatment followed by a peroxide treatment.

The use of an alkaline hydrogen peroxide solution as a delignifying and brightening agent for unbleached kraft and sulphite pulp is known. The optimum conditions for the use of alkaline hydrogen peroxide have been reported for softwood pulp to be: consistency 10-20%, retention time 2 hours, temperature 80-100°C, NaOH charge 2.5% on pulp and 1% hydrogen peroxide on pulp, oven-dry basis. By applying these conditions, it is possible to decrease a Kappa number from the original value of 30 to about 18 on a softwood kraft pulp.

The use of peroxide in the first alkaline extraction stage, first reported in 1946 and subsequently in other articles, has been practised at some mills with successful decolorization of pulp. The treatment relieves the usual drop in brightness during the conventional extraction stage.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improvement in the delignification/bleaching process of a chemical pulp wherein the pulp is treated with an oxygen-containing gas without requiring a highly pressurized vessel.

It is a further object of the present invention to provide an improvement in the delignification/bleaching of a chemical pulp wherein the pulp is delignified while minimizing pulp degradation.

The above mentioned objects are attained in the present invention by the use of two improvements in the pulp delignification/bleaching process. By the first and most important improvement washed pulp from the chemical digester is subjected to a simultaneous reaction of a peroxygen compound, an alkali compound and an oxygen containing gas under certain preferred process conditions. Surprisingly, by this simultaneous reaction, one is able to delignify and brighten the pulp at low operating pressure and minimize its degradation. Minimal modification to existing plant equipment is necessary thus making the new process economically and commercially viable.

The second improvement involves the treatment of a washed chlorinated pulp which comprises subjecting the pulp to the simultaneous reaction of a peroxygen compound, an alkali compound and an oxygen containing gas under desired process conditions.

The two improvements of the present invention can be combined for even greater effect. In this instance, the pulp is first delignified using the first improvement set forth above, and then the washed pulp is treated in a chlorination stage (C, C/D or D/C) with C referring to the use of chlorine alone, C/D to a chlorination stage where 5 to 30% of the total active chlorine is placed by chlorine dioxide, and D/C where 30 to 70% of the total active chlorine is replaced by chlorine dioxide. Subsequently, the washed chlorinated pulp is subjected to the step of the second improvement as per the above.

The present invention is applicable to any chemical cellulosic pulp (i.e. kraft, soda or sulphite) and can be used with both softwood or hardwood pulp and/or other varieties of fibrous non-woody lignocellulose material such as, for example, bagasse or hemp.

DETAILED DESCRIPTION OF THE INVENTION

In a first aspect of the present invention, there is provided in a delignification/bleaching process the improvement comprising the step of simultaneously treating a lignin containing, chemically cooked, washed pulp with 0.5% to 4% of an alkali compound, 0.1 to 2% of a peroxygen compound, and 0.4 to 0.6% of an oxygen gas at a partial pressure of between 0.01 to 0.4 MPa, in the presence of a catalyst to prevent the reduction of viscosity, at a temperature of between 40-95°C for a time between 1 minute to 120 minutes at a pulp consistency of between 5% and 25%. All measurements stated herein are by weight on an oven-dry pulp basis.

In a second aspect of the present invention, there is provided an improvement in a process for brightening pulp which has been treated according to the first aspect herein above and subsequently treated with a chlorine containing compound and washed, the improvement comprising the step of treating the washed chlorinated pulp simultaneously with 0.5% to 4% of an alkali compound, 0.1 to 1% of a peroxygen compound, and 0.1 to 3% of an oxygen containing gas at 0.1 to 0.4 MPa, at a temperature of between 50-90°C for a period of between 3 to 120 minutes at a pulp consistency of between 5% and 25%.

In a third aspect of the present invention, there is provided an improvement in a delignification/bleaching process comprising the step of treating a washed chlorinated pulp simultaneously with 0.5% to 4% of an alkali compound, 0.1 to 1.0% of a peroxygen compound, and 0.1 to 3% of an oxygen containing gas at 0.1 to 0.4 MPa, at a temperature of between 50-90°C for a period of between 3 to 120 minutes at a pulp consistency of between 5% and 25%.

Prior to the delignification stage, an acid treatment and/or a washing step to remove any black liquor from the pulp may be carried out and after the delignification stage, a washing step to remove the reaction products is utilized.

The compounds utilized in the improvements of the present invention may be selected from those well known in the art. Thus, for example, the peroxygen compound may include conventional inorganic peroxides such as hydrogen and sodium or an organic peroxide such as benzoyl peroxide, tertiary-butyl hydroperoxide, and peracetic acid.

Conventionally used alkali compounds include sodium hydroxide, sodium carbonate, calcium carbonate, magnesium carbonate, magnesium hydroxide, etc.

In a preferred embodiment of the first aspect of this invention, the alkaline compound, preferably sodium hydroxide, is utilized in charges ranging from 1.0 to 3.5 by weight of oven-dried pulp. The peroxygen compound is preferably charged at 0.5 to 1.8% by weight and the oxygen at between 0.5 to 2.2% by weight. A preferred catalyst is magnesium sulphate which can be added in charges ranging between 0.1 to 1% by weight. The oxygen is introduced and maintained at a pressure of between 0.1 to 0.3 MPa for a preferred time range of between 3 to 30 minutes. The preferred ranges of temperature, total time and pulp consistency will be between 70-95°C, 3-60 minutes and 9 to 15% respectively. The pH at the end of the treatment will normally be between 9.5 to 12.

Following the delignification, the pulp is subjected to a normal washing step to remove the reaction products.

In a preferred embodiment of the second aspect of the invention, the alkaline compound, preferably sodium hydroxide, is utilized in charges ranging from 2 to 3.5% by weight of oven-dry pulp. The peroxygen compound is preferably charged at between 0.2 and 0.7% by weight and the oxygen at between 0.4 to 0.6% by weight at a pressure of between 0.1 to 0.3 MPa. Preferred process conditions are: consistency of between 8 to 20%, a time of between 3 to 30 minutes and a temperature of 60 to 90°C. As in the first aspect of the invention a viscosity protecting catalyst such as the magnesium ion in the amount of between 0.1 and 1.0% by weight can be beneficially used.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graph illustrating various alkali delignification procedures plotting the Kappa number of the pulp versus the time; and

FIGURE 2 is a graph of the alkali delignification procedures of Figure 1 plotting viscosity versus time.

As an example of the first treatment, unbleached kraft pulp from coniferous wood, having a Kappa number of 26.6 and 0.5% cuene viscosity of 26.3 mPa.s was used in the following experiments to test alkaline delignification treatments. The results are shown in Table I and summarized in Figures 1 and 2. In each of examples 1 to 5, samples of pulp were removed at time intervals of 15, 30, 60 and 120 minutes, washed, and the Kappa number and viscosity determined.

Example 1

Treatment with NaOH alone

One portion of the unbleached pulp was treated with a solution containing 2.5% NaOH on pulp, OD basis, mixed at 10% consistency and a temperature of 80°C.

Example 2

Treatment with NaOH and H_2O_2

One portion of the unbleached pulp was treated with a solution containing 2.5% NaOH, I% H_2O_2 and 0.5% $MgSO_4$ on pulp, OD basis, and mixed at 10% consistency and temperature of 80°C.

Example 3

Treatment with NaOH and Oxygen at an Oxygen Pressure of 14 MPa.

One portion of the unbleached pulp was treated with a solution containing 2.5% NaOH and 0.5% $MgSO_4$ on pulp, OD basis, then gaseous oxygen was added and mixed at 10% consistency and a temperature of 80°C and held at one oxygen pressure of 0.14 MPa.

Example 4

Treatment with NaOH and Oxygen at an Oxygen Pressure of 0.50 MPa.

One portion of the unbleached pulp was treated with a solution containing 2.5% NaOH, and 0.5% $MgSO_4$ on pulp, OD basis, and mixed at 10% consistency and a temperature of 80°C, and held at an oxygen pressure of 0.50 MPa.

The effects of different alkaline delignification treatments on Kappa number and viscosity are shown in Table I and Figures 1 and 2. At a fixed 2.5% NaOH charge, consistency 10%, temperature 80°C, mixing intensity 30 rpm, for a reaction time of 30 minutes, the Kappa number was decreased by 14, 24, 38 and 45% in treatments with NaOH alone, H_2O_2 and NaOH, NaOH and oxygen at 0.14 MPa, and NaOH and oxygen at 0.50 MPa, respectively. Increasing the retention time to 120 minutes from 30 minutes did not substantially further decrease the Kappa number. Viscosity decreased by 30% from initial value in the 30-minute reaction provided that Mg++ ion was used as protection.

Example 5

Treatment with NaOH, H_2O_2 and Oxygen at an Oxygen Pressure of 0.14 MPa.

An unexpected result was obtained when NaOH, H_2O_2, and oxygen (pressure of oxygen at 0.14 MPa) were mixed into the unbleached pulp in one treatment. The results in Table I and Figures 1 and 2 show that delignification of the pulp to a Kappa number of 15.0 (a decrease of 44%) and a 0.5% cuene viscosity of 21.1 mPa.s (a decrease of 20%) was obtained in a 15-minute reaction, a pulp consistency of 10%, a temperature of 80°C, and using the following chemical charges expressed as percentage on pulp, OD basis: NaOH, 2.5%; H_2O_2, 1.0%; $MgSO_4$, 0.5%.

TABLE I

COMPARISON BETWEEN DIFFERENT ALKALINE DELIGNIFICATIONS OF A SOFTWOOD KRAFT PULP

Unbleached Kappa No. 26.6; Viscosity 26.3 mPa.s, Brightness 32.5% ISO

EXAMPLE		CHEMICAL ON PULP, OD BASIS			OXYGEN PRESSURE MPa	TIME MIN.	FINAL pH	KAPPA NO.	0.5%-CUENE VISCOSITY mPa.s	BRIGHTNESS % ISO
		NaOH	H_2O_2	$MgSO_4$						
1	a	2.5	-	-	-	15	12.2	24.7	23.8	32.9
	b	2.5	-	-	-	30	12.1	23.4	22.7	33.7
	c	2.5	-	-	-	60	12.1	22.5	21.6	34.6
	d	2.5	-	-	-	120	12.1	22.5	21.2	35.5
2	a	2.5	1.0	0.5	-	15	11.9	22.1	22.5	35.8
	b	2.5	1.0	0.5	-	30	11.8	20.3	21.9	36.4
	c	2.5	1.0	0.5	-	60	11.8	18.8	19.7	39.3
	d	2.5	1.0	0.5	-	120	11.6	17.7	19.1	39.9
3	a	2.5	-	0.5	0.14	15	11.9	18.7	21.5	39.5
	b	2.5	-	0.5	0.14	30	11.9	16.6	20.8	42.3
	c	2.5	-	0.5	0.14	60	11.7	14.4	18.9	48.2
	d	2.5	-	0.5	0.14	120	11.4	13.5	18.0	51.2
4	a	2.5	-	0.5	0.50	15	10.8	16.5	19.9	42.9
	b	2.5	-	0.5	0.50	30	10.7	14.7	18.2	45.2
	c	2.5	-	0.5	0.50	60	10.7	14.0	17.2	49.0
	d	2.5	-	0.5	0.50	120	10.6	13.2	16.4	51.8
5	a	2.5	1.0	0.5	0.14	15	11.9	15.0	21.1	46.9
	b	2.5	1.0	0.5	0.14	30	11.7	12.9	19.9	51.9
	c	2.5	1.0	0.5	0.14	60	11.6	12.7	18.7	50.9
	d	2.5	1.0	0.5	0.14	90	11.5	12.0	18.7	52.3

As will be seen from the above examples, and as shown in Figures 1 and 2, the treatment of the present invention improves the extent of the delignification of the pulp as measured by the Kappa number. At the same time, less pulp degradation occurs as measured by the viscosity. Thus, significantly, the hydrogen peroxide and oxygen at the low pressure provides better results than the oxygen delignification at the higher pressure without the peroxide.

In the second aspect of the invention, the alkaline/peroxide/oxygen treatment is employed with a pulp that has been semi-delignified. This pulp may be delignified in a conventional manner or in the manner taught herein. Prior to the present treatment (hereinafter designated as an EPO stage or an X stage, the pulp is normally subjected to a chlorine or chlorine dioxide treatment.

The present invention can conveniently be practiced using an oxygen containing gas which along with the lignocellulose containing material and alkaline and peroxide compounds are mixed by a mixer installed immediately before either an upflow tower or an upflow retention tube prior to entering into a downflow tower.

As was the case in the first treatment stage, the compounds utilized in the practice of the present invention may be selected from those well known to those skilled in the art. Thus, for example, the peroxygen compound employed in the extraction stage may include an inorganic peroxide such as hydrogen or sodium peroxide and organic peroxides such as benzoyl peroxide and tertiary-butyl hydroperoxide. Typically, the alkali may be sodium hydroxide, sodium carbonate or magnesium carbonate.

Preferred ranges of treatment for carrying out the third aspect of the invention include using the peroxygen compound at between 0.2 to 0.7% by weight of oven-dried pulp, the hydroxide compound at between 2 to 3.5% by weight and oxygen at between 0.4 to 0.6% by weight. The oxygen pressure is preferably maintained at between 0.05 to 0.15 MPa and process parameters are a temperature range of between 40°C to 90°C and a 3 to 30 minute reaction time with a consistency of between 8% to 20%.

Examples of the above treatment are given hereinbelow.

Example 6

An unbleached softwood kraft pulp, Kappa number 35, 0.5% cuene viscosity, 39 mPa.s was divided into 3 samples. One sample of the unbleached sample was chlorinated with chorine alone, under conditions shown in Table II.

Example 7

The second sample was chlorinated with a mixture of chlorine and chlorine dioxide where the chlorine dioxide replaced 7% of the chlorine charge.

Example 8

The third sample of pulp was chlorinated sequentially with chlorine dioxide and chlorine. The chlorine dioxide replaced 40% of the total chlorine charge.

After washing each sample from examples 1, 2 and 3, they were equally subdivided into 6 portions:

one portion extracted with sodium hydroxide -E

another portion extracted with sodium hydroxide + hypochlorite -(EH)

another portion extracted with sodium hydroxide + peroxide -(EP)

another portion extracted with sodium hydroxide + oxygen -(EO)

another portion extracted with sodium hydroxide + peroxide + oxygen -(EPO) or X

another portion extracted with sodium hydroxide + hypochlorite + oxygen -(EHO)

Conditions and results of the experiments are shown in Table II.

The combination of alkaline hydroxide, peroxide and oxygen improved the extent of delignification as measured by the Kappa number in each group of the different chlorinated pulps. The brightness of the peroxide-oxidative extraction treated pulp was substantially higher than that obtained after other oxidative extractions.

A Novel Bleaching Sequence XC/DXD

A combination of sodium hydroxide, peroxide, and oxygen was used as a predelignification stage and as peroxide oxidative extraction stage (each designated as an (EPO) or an X stage) following a chlorination stage.

Example 9

A softwood kraft pulp, Kappa number 26.6, 0.5% cuene viscosity 26.3 mPa.s was treated in an X delignification stage at 10% consistency by simultaneously treating the pulp in the presence of hydrogen peroxide, sodium hydroxide, magnesium sulphate, and oxygen at a pressure of 0.14 MPa. The conditions are listed in Table III.

After washing the chlorinated pulp, the pulp was divided into three portions and extracted in the following manner using conditions described in Tables II and III:

One portion was extracted with sodium hydroxide -E;

Another portion was extracted with sodium hydroxide and oxygen -(EO);

The third portion was extracted with sodium hydroxide, hydrogen peroxide and oxygen -X.

Each extracted pulp was washed and the Kappa number, viscosity and brightness were measured. The results are listed in Table III. The brightness of the XC/DX-treated pulp reached 77.5% ISO, which was some 20 points higher than the XC/D(EO)-treated pulp.

Each extracted sample of pulp was then divided into 4 equal portions and each portion was treated with a different charge of chlorine dioxide using conditions listed in Table III. The brightness obtained for each sample along with the viscosities are shown in Table III. The superiority of the XC/DXD-treatment is shown in that a 91.3% ISO brightness was obtained using 0.40% chlorine dioxide (oven-dry basis) in the D stage, whereas after XC/DED and XC/D(EO)D, the brightnesses were 88.0 and 89.8% ISO, respectively. By increasing the chlorine dioxide charge to 0.60% on pulp in the D stage, the brightness ceiling of the pulp became greater than 92% ISO after XC/DXD, which was not achieved even at high chlorine dioxide charges in the D stage of an XC/DED and an XC/D(EO)D sequence.

Examples 10 and 11

These examples show the use of an (EPO) bleaching stage in an OC/D(EPO)D bleaching sequence on a softwood and hardwood kraft pulp respectively. The results of the oxygen delignification stage without peroxide in an OC/DXD sequence are set forth in Tables IV and V respectively. This sequence produced a bleached pulp with good brightnesses, but with viscosities that were inferior to those after XC/DXD bleaching. An X delignification step is desirable since the oxygen pressure can be lower as well as the time requirement.

TABLE II

THE USE OF OXIDATIVE REAGENTS IN THE E_1 STAGE

SEQUENCE	CHEMICAL ON PULP OD BASIS, % of							KAPPA NO.	0.5% CUENE VISCOSITY, mPa.s	BRIGHT-NESS, % ISO
	Cl_2	ClO_2	NaOH	NaOCl	H_2O_2	O_2	$MgSO_4$			
Example 6										
CE	6.8	-	4.0	-	-	-	-	6.2	32	30
C(EH)	6.8	-	4.0	1.0	-	-	-	5.9	32	42
C(EP)	6.8	-	4.0	-	0.5	-	-	5.8	32	34
C(EO)	6.8	-	4.0	-	-	0.5	-	4.2	29	42
C(EPO)	6.8	-	4.0	-	0.5	0.5	0.10	2.8	29	70
C(EHO)	6.8	-	4.0	1.0	-	0.5	-	4.7	22	48
Example 7										
C/DE	6.3	0.2	4.0	-	-	-	-	6.2	35	32
C/D(EH)	6.3	0.2	4.0	1.0	-	-	-	5.3	31	42
C/D(EP)	6.3	0.2	4.0	-	0.5	-	-	5.1	33	33
C/D(EO)	6.3	0.2	4.0	-	-	0.5	-	4.0	30	42
C/D(EPO)	6.3	0.2	4.0	-	0.5	0.5	0.10	2.8	30	71
C/D(EHO)	6.3	0.2	4.0	1.0	-	0.5	-	4.5	26	47

TABLE II (cont'd)

SEQUENCE	CHEMICAL ON PULP OD BASIS, % of Cl_2	ClO_2	NaOH	NaOCl	H_2O_2	O_2	$MgSO_4$	KAPPA NO.	0.5% CUENE VISCOSITY, mPa.s	BRIGHT-NESS % ISO
Example 8										
(DC)E	4.2	1.1	3.5	-	-	-	-	5.2	39	39
(DC)(EH)	4.2	1.1	3.5	1.0	-	-	-	4.8	32	68
(DC)(EP)	4.2	1.1	3.5	-	0.5	-	-	4.8	34	67
(DC)(EO)	4.2	1.1	3.5	-	-	0.5	-	3.9	30	54
(DC)(EPO)	4.2	1.1	3.5	-	0.5	0.5	0.10	2.7	28	76
(DC)(EHO)	4.2	1.1	3.5	1.0	-	0.5	-	4.4	26	69

Unbleached Kappa No. 35.0, Viscosity 39 mPa.s.

Chlorination Stages	Consistency %	Temperature °C	Time Min.
C	3.5	20	30
C/D	3.5	50	6
(DC)D	10	60	1
C	3.5	90	30

Extraction Stages

E, no oxygen
(EO), (EPO), (EHO),
0.14 MPa oxygen pressure
Consistency 10%,
Temperature 60°C., Time 60 minutes.

TABLE III

XC/DED, XC/D(EO)D AND XC/DXD BLEACHING SEQUENCES
X = COMBINATION ALKALINE-PEROXIDE-OXYGEN TREATMENT
ON AN UNBLEACHED COMMERCIAL SOFTWOOD KRAFT PULP

Kappa number 26.6, 0.5% Cuene, Viscosity 26.3 mPa.s

Example 9

(EPO) OR X STAGE	
NaOH on pulp, %	2.2
$MgSO_4$ on pulp, %	0.5
H_2O_2 on pulp, %	1.0
O_2 pressure, MPa	0.14
O_2 time, min	5
Total time, min	30
Temperature, °C	80
Pulp consistency, %	10
pH	10.9
Kappa number	12.6
Viscosity, mPa.s	19.9

CHLORINATION STAGE	
Cl_2 added, %	2.49
ClO_2 added, %	0.11
Total active chlorine, %	2.77
Time, min	30
Temperature, °C	25
Consistency, %	3
pH	2.2

E, (EO) OR X STAGE	E	(EO)	(EPO) OR X
NaOH, on pulp, %	1.52	1.52	1.52
$MgSO_4$ on pulp, %	0	0	0.10
H_2O_2 on pulp, %	0	0	0.50
O_2 pressure, MPa	0	0.14	0.14
O_2 time, min	0	3.0	3.0
Total time, min	60	60	60

TABLE III (cont'd)

E, (EO) OR X STAGE	E	(EO)	(EPO) OR X
Temperature, °C	72	72	72
Pulp consistency	10	10	10
pH	11.2	10.8	10.7
Kappa number	2.5	1.9	1.1
Viscosity, mPa.s	22.6	22.4	20.2
Brightness, % ISO	42.6	57.6	77.5

PREVIOUS TREATMENT XC/DE

D STAGE	A	B	C	D
ClO_2 added on pulp %	0.40	0.60	0.80	1.00
ClO_2 consumed on pulp %	0.40	0.60	0.78	0.84
Time, min	180	180	180	180
Temperature, °C	70	70	70	70
Consistency, %	10	10	10	10
End pH	3.6	3.6	3.5	3.6
Brightness, % ISO	88.0	89.8	89.9	90.1
Viscosity, mPa.s	19.8	19.1	18.9	18.3

PREVIOUS TREATMENT XC/D (EO)

D STAGE	E	F	G	H
ClO_2 added on pulp %	0.40	0.60	0.80	1.00
ClO_2 consumed on pulp %	0.40	0.50	0.57	0.60
Time, min	180	180	180	180
Temperature, °C	70	70	70	70
Consistency, %	10	10	10	10
End pH	3.4	3.4	3.4	3.4
Brightness, % ISO	89.8	90.4	90.6	91.1
Viscosity, mPa.s	19.8	19.9	19.8	18.1

PREVIOUS TREATMENT XC/DX

D STAGE	I	J	K	L
ClO_2 added on pulp, %	0.40	0.60	0.80	1.00
ClO_2 consumed on pulp %	0.27	0.34	0.42	0.44
Time, min	180	180	180	180
Temperature °C	70	70	70	70
Consistency	10	10	10	10
End pH	3.4	3.5	3.5	3.5
Brightness, % ISO	91.3	92.2	92.2	92.3
Viscosity, mPa.s	19.4	19.3	19.3	18.8

TABLE IV

THE USE OF AN (EPO) BLEACHING STAGE IN AN OC/D(EPO)D BLEACHING SEQUENCE ON UNBLEACHED SOFTWOOD KRAFT PULP

Kappa number 26.6, Viscosity 26.3 mPa.s. Brightness 32.5% ISO

Example 10

OXYGEN DELIGNIFICATION	
NaOH on pulp, %	2.2
$MgSO_4$ on pulp, %	0.5
0_2 on pulp, %	1.4
0_2 pressure, MPa	0.68
0_2 time, min	60
Total time, min	60
Temperature, °C	80
Pulp consistency, %	10
pH	10.6
Kappa number	14.0
Viscosity, mPa.s	17.2

CHLORINATION STAGE	
Cl_2 added, %	2.77
$Cl0_2$ added, %	0.12
Total active chlorine %	3.08
Time, min	30
Temperature, °C	25
Consistency, %	3
pH	1.8

E, (EO) OR X STAGE	E	(EO)	(EPO) OR X
NaOH on pulp, %	1.8	1.8	1.80
$MgSO_4$ on pulp, %	0	0	0.10
H_20_2 on pulp, %	0	0	0.50
0_2 charge on pulp	0	0.5	0.5
0_2 pressure, MPa	0	0.14	0.14
0_2 time min	0	3.0	3.0
Total time, min	60	60	60

TABLE IV (cont'd)

E, (EO) OR X STAGE	E	(EO)	(EPO) OR X
Temperature, °C	72	72	72
Pulp consistency	10	10	10
pH	11.1	10.7	10.6
Kappa number	2.6	1.9	1.0
Viscosity, mPa.s	18.3	18.0	17.4
Brightness, % ISO	42.8	58.0	78.3

PREVIOUS TREATMENT OC/DE D STAGE	A	B	C	D
ClO_2 added on pulp %	0.40	0.60	0.80	1.0
ClO_2 consumed on pulp %	0.40	0.60	0.80	0.86
Time, min	180	180	180	180
Temperature, °C	60	60	60	60
Consistency, %	10	10	10	10
End pH	3.5	3.5	3.6	3.5
Brightness, % ISO	88.3	90.0	90.0	90.3
Viscosity, mPa.s	16.6	16.2	16.2	16.0
PREVIOUS TREATMENT OC/D(EO) D STAGE	**E**	**F**	**G**	**H**
ClO_2 added on pulp %	0.40	0.60	0.80	1.00
ClO_2 consumed on pulp %	0.40	0.52	0.53	0.58
Time, min	180	180	180	180
Temperature, °C	60	60	60	60
Consistency, %	10	10	10	10
End pH	3.3	3.4	3.4	3.4
Brightness, % ISO	90.2	90.6	90.8	91.6
Viscosity, mPa.s	16.3	16.1	16.2	15.9
PREVIOUS TREATMENT OC/DX D STAGE	**I**	**J**	**K**	**L**
ClO_2 added on pulp %	0.40	0.60	0.80	1.00
ClO_2 consumed on pulp %	0.31	0.36	0.46	0.49
Time, min	180	180	180	180
Temperature, °C	60	60	60	60
Consistency, %	10	10	10	10
End pH	3.5	3.5	3.5	3.5
Brightness, % ISO	91.4	92.6	92.6	92.8
Viscosity, mPa.s	16.0	15.9	15.8	15.9

TABLE V

THE USE OF AN (EPO) BLEACHING STAGE IN AN OC/D(EPO)D BLEACHING SEQUENCE ON UNBLEACHED HARDWOOD KRAFT PULP

Kappa number 17.7, Viscosity 22.3 mPa.s, Brightness 36.0% ISO

Example 11

OXYGEN DELIGNIFICATION	
NaOH on pulp, %	2.0
$MgSO_4$ on pulp, %	0.5
O_2 on pulp, %	1.2
O_2 pressure, MPa	0.68
O_2 time, min	30
Total time, min	30
Temperature, °C	110
Pulp consistency, %	10
pH	10.4
Kappa number	9.8
Viscosity	17.9

CHLORINATION STAGE	
Cl_2 added, %	1.9
ClO_2 added, %	0.8
Total active chlorine %	2.1
Time, min	30
Temperature, °C	22
Consistency, %	3
pH	1.8

E, (EO) OR X STAGE	E	(EO)	(EPO) OR X
NaOH, on pulp, %	1.3	1.3	1.3
$MgSO_4$ on pulp, %	0	0	0.1
H_2O_2 on pulp, %	0	0	0.50
O_2 charge on pulp	0	0.5	0.5
O_2 pressure, MPa	0	0.14	0.14
O_2 time, min	0	3.0	3.0
Total time, min	60	60	60

TABLE V (cont'd)

E, (EO) OR X STAGE	E	(EO)	(EPO) OR X
Temperature, °C	60	60	60
Pulp consistency	10	10	10
pH	11.2	10.8	10.9
Kappa number	2.4	1.8	0.9
Viscosity, mPa.s	16.3	16.1	15.9
Brightness, % ISO	47.2	61.3	79.2

PREVIOUS TREATMENT OC/DE D STAGE	A	B	C	D
ClO_2 added on pulp %	0.4	0.6	0.8	1.0
ClO_2 consumed on pulp %	0.30	0.35	0.39	0.42
Time, min	180	180	180	180
Temperature, °C	60	60	60	60
Consistency, %	10	10	10	10
End pH	3.9	3.9	4.0	4.1
Brightness, % ISO	92.2	92.3	92.6	92.8
Viscosity, mPa.s	15.7	15.5	15.6	15.3

PREVIOUS TREATMENT OC/D(EO) D STAGE	E	F	G	H
ClO_2 added on pulp %	0.4	0.6	0.8	1.0
ClO_2 consumed on pulp %	0.27	0.31	0.33	0.35
Time, min	180	180	180	180
Temperature, °C	60	60	60	60
Consistency, %	10	10	10	10
End pH	4.0	4.1	4.1	4.1
Brightness, % ISO	92.9	93.1	93.1	93.3
Viscosity, mPa.s	15.7	15.2	15.0	15.1

PREVIOUS TREATMENT OC/DX D STAGE	I	J	K	L
ClO_2 added on pulp %	0.4	0.6	0.8	1.0
ClO_2 consumed on pulp %	0.22	0.26	0.30	0.31
Time, min	180	180	180	180
Temperature, °C	60	60	60	60
Consistency, %	10	10	10	10
End pH	4.1	4.2	4.1	4.1
Brightness, % ISO	93.6	93.7	93.8	93.8
Viscosity, mPa.s	15.6	15.1	15.0	15.0

It will be understood that the above-described embodiments and examples are for purposes of illustration only and that changes and modifications may be made thereto without departing from the spirit and scope of the invention.

Claims

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a pulping process wherein a cellulosic material is subjected to a chemical cook, characterized by the step of simultaneously treating the cooked pulp with:

(a) 0.5 to 4% by weight of an alkali compound;

(b) 0.1 to 2% by weight of a peroxygen compound;

(c) 0.4 to 6% by weight of an oxygen gas at a partial pressure of 0.01 to 0.4 MPa; and

(d) a viscosity protecting catalyst,

said treatment being carried out at a temperature of between 40°C to 95°C for a time between 1 minute to 120 minutes at a pulp consistency of between 5% to 25%, all measurements being on an oven-dry pulp basis.

2. The process of claim 1 characterized by said viscosity protecting catalyst being a magnesium ion present at between 0.1 to 1.0% by weight.

3. The process of claim 1, characterized by the cellulosic material being selected from the group consisting of softwood and hardwoods.

4. The process of claim 1, characterized by the alkali compound being selected from the group consisting of sodium hydroxide, sodium carbonate, calcium carbonate and magnesium carbonate, and said peroxide compound being selected from the group consisting of hydrogen peroxide, sodium peroxide, benzoyl peroxide, tertiary-butyl hydroperoxide and peracetic acid.

5. In a process for brightening pulp which includes the steps of semi-delignifying the pulp, treating the semi-delignified pulp with a chlorine-containing compound and subsequently washing the chlorine treated pulp, characterized by the step of subsequently treating the washed chlorinated pulp simultaneously with:

(a) 0.5 to 4% by weight of an alkali compound;

(b) 0.1 to 1% by weight of a peroxygen compound; and

(c) 0.1 to 3% by weight of an oxygen-containing gas at a pressure of between 0.1 to 0.4 MPa;

(d) a viscosity protecting catalyst,

said treatment being carried out at a temperature of between 50°C to 90°C for a period of time between 3 to 120 minutes at a pulp consistency of between 5% and 25%, all measurements by weight being based on an oven-dry pulp basis.

6. The method of claim 5 characterized by said viscosity protecting catalyst being a magnesium ion present at between 0.1 to 1.0% by weight.

7. The method of claim 6, characterized by said alkali compound being selected from the group consisting of sodium hydroxide, sodium carbonate, calcium carbonate and magnesium carbonate, and said peroxide compound is selected from the group consisting of hydrogen peroxide, sodium peroxide, benzoyl peroxide, tertiary-butyl hydro-peroxide and peracetic acid.

8. In a chemical cellulosic pulping process wherein the pulp is subjected to a chemical cook, characterized by the steps of:

A) simultaneously treating the cooked pulp with:

(i) 0.5 to 4% by weight of an alkali compound;

(ii) 0.1 to 2% by weight of a peroxygen compound;

(iii) 0.4 to 6% by weight of an oxygen gas at a partial pressure of 0.01 to 0.4 MPa; and

(iv) a viscosity protecting catalyst,

said treatment being carried out a temperature of betwen 40°C to 95°C for a time between 1 minute to 120 minutes at a pulp consistency of between 5% to 25%, all measurements being on an oven-dry pulp basis;

B) treating the delignified pulp with a chlorine-containing compound;

C) washing the chlorinated pulp; and

D) simultaneously treating the washed chlorinated pulp with:

(i) 0.5 to 4% by weight of an alkali compound;

(ii) 0.1 to 1% by weight of a peroxygen compound; and

(iii) 0.1 to 3% by weight of an oxygen-containing gas at a pressure of between 0.1 to 0.4 MPa; and

(iv) a viscosity protecting catalyst,

said treatment being carried out at a temperature of between 50°C to 90°C for a period of time between 3 to 120 minutes at a pulp consistency of between 5% and 25%, all measurements by weight being based on an oven-dry pulp basis.

9. The process of claim 8 characterized by the alkali compound in steps A and D being selected from the group consisting of sodium hydroxide, sodium carbonate, calcium carbonate and magnesium carbonate, and said peroxide compound being selected from the group consisting of hydrogen peroxide, sodium peroxide, benzoyl peroxide, tertiary-butyl hydro-peroxide and peracetic acid; and said viscosity protecting agent is the magnesium ion.

10. The process of claim 1, wherein said pulp has been subjected to a chemical cook selected from the group consisting of kraft, soda and sulphite cooks.

11. The process of claim 5, wherein said pulp has been subjected to a chemical cook selected from the group consisting of kraft, soda and sulphite cooks.

12. The process of claim 8, wherein said pulp has been subjected to a chemical cook selected from the group consisting of kraft, soda and sulphite cooks.

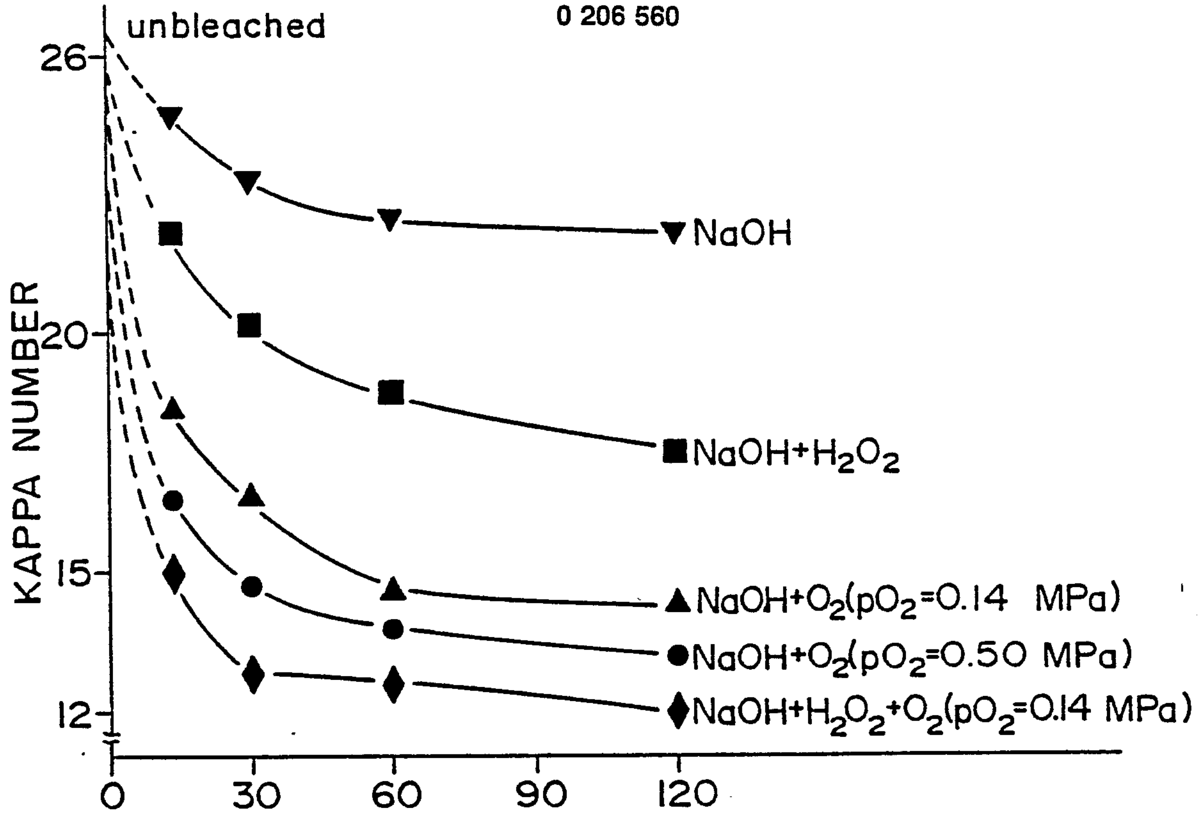
unbleached
KAPPA NUMBER
26
20
15
12
0
30
60
90
120
TIME, MINUTES
▼NaOH
■NaOH+H2O2
▲NaOH+O2(pO2=0.14 MPa)
●NaOH+O2(pO2=0.50 MPa)
♦NaOH+H2O2+O2(pO2=0.14 MPa)

FIG. 1

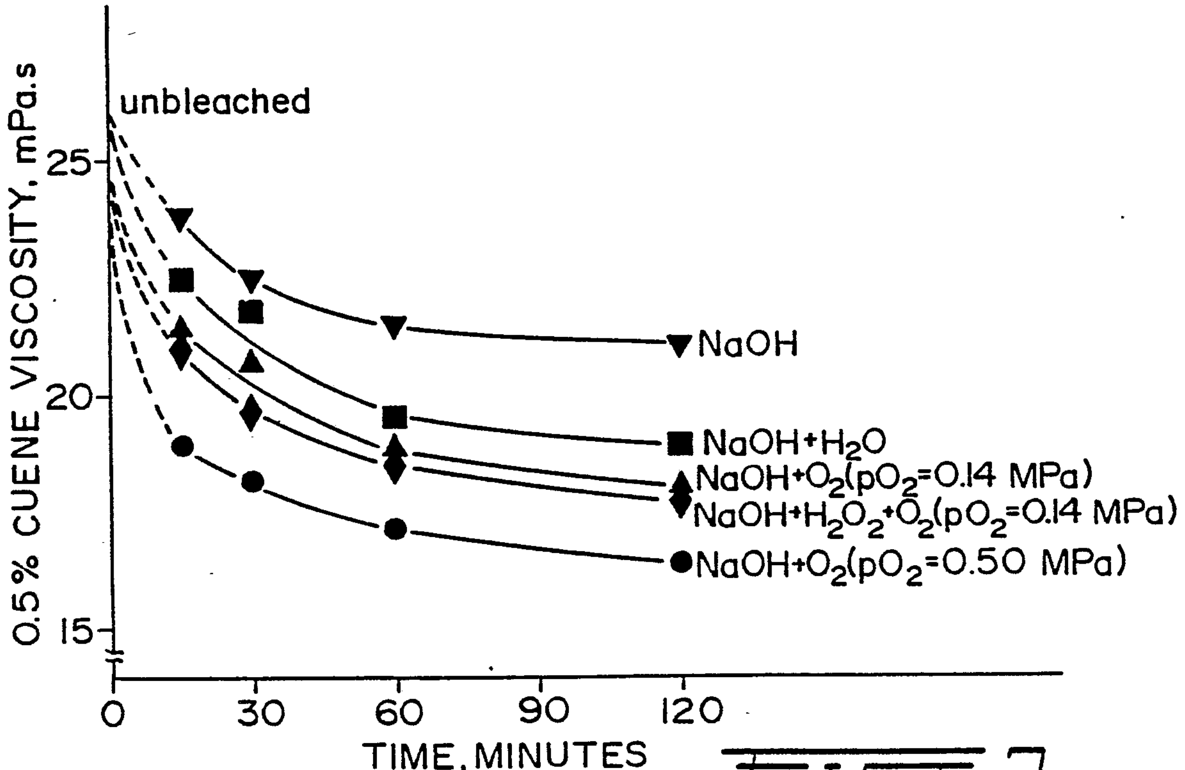
unbleached
0.5% CUENE VISCOSITY, mPa.s
25
20
15
0
30
60
90
120
TIME, MINUTES
▼NaOH
■NaOH+H2O
▲NaOH+O2(pO2=0.14 MPa)
♦NaOH+H2O2+O2(pO2=0.14 MPa)
●NaOH+O2(pO2=0.50 MPa)

FIG. 2