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<p>(54) Title: AN IMPROVED METHOD FOR BLEACHING PULP</p>		
<p>(57) Abstract</p> <p>A method of bleaching pulp of cellulosic fibrous material in the production of chemical pulp, fed continuously through a bleaching line, is bleached with ozone and at least one member of the group of bleaching agents consisting of chlorine dioxide, chlorine, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides, wherein this bleaching occurs in a single stage and wherein this single stage does not contain an intermediate washing or extraction stage and wherein the redox potential of the pulp immediately after the addition of each bleaching agent is brought down to a level of 0 to about 20 % of the original value of the redox potential prior to the addition of the subsequent bleaching agent is disclosed.</p>		

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AN IMPROVED METHOD FOR BLEACHING PULP

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of bleaching pulp of cellulosic
5 fibrous material in the production of chemical pulp wherein the entering pulp is fed
continuously in a bleaching line and bleached with a plurality of bleaching agents
comprising ozone and at least one member of the group consisting of chlorine dioxide
(D), chlorine (C), hypochlorite (H), acidic hydrogen peroxide (Pa), peracetic acid (PAA),
persulfuric acid (Ca), and organic peroxides (RO).

Description of the Prior Art

Chlorine and hypochlorite are common bleaching agents employed in the
bleaching of pulp for cellulosic fibrous material, particularly chemical pulp.
Unfortunately, in such a process these chlorine products readily form a variety of
chlorinated organic compounds, which are known to have a significant detrimental
15 impact on the environment and to leave readily detectable levels in the final bleached
pulp, as well. Accordingly, there has been increasing resistance to the use of chlorine in
pulp bleaching.

This resistance has resulted in and will likely continue to result in the
lowering of maximum emission amounts of chlorinated organic substances in the
20 bleaching process and the bleached pulp. The maximum emission values are commonly
measured in kilograms of adsorbable organic halogen (AOX) per ton pulp. Until about
the year 2000, a maximum level of 1.0 to 2.0 kg AOX per ton dry pulp will probably be
an acceptable limit under environmental regulations. However, thereafter, and possibly
earlier if technologically feasible, a maximum limit of less than 1.0 kg AOX per ton pulp
25 is likely to be established.

Several options have been proposed or practiced in the prior art to reduce
or eliminate chlorinated organics in the bleaching process. The most straightforward
method is to substitute non-chlorine bleaching chemicals, such as oxygen, peroxides,

ozone, peracetic acid, among others, for chlorine-based bleaching chemicals.

Unfortunately, cost concerns may make such an alternative unfeasible.

Another option to reduce the discharge of chlorinated organic compounds is to lower chlorine usage in the first stage of the bleaching process. Two alternatives that produce no significant degradation of pulp properties have been commercially employed for this purpose. These are (a) extended delignification in the pulp cooking stage and (b) oxygen delignification. These alternatives, with proper extraction, reduce the lignin content of brown stock going into the bleach plant. Nonetheless, even greater reductions in chlorine usage may be necessary.

A third option to reduce production of chlorinated organics in the bleaching process is to substitute chlorine dioxide for chlorine. Chlorine dioxide is a relatively strong oxidant compared to chlorine. To achieve the same degree of delignification, it requires only about thirty-eight weight percent chlorine dioxide on the pulp compared with one hundred weight percent of chlorine. However, prior art processes using such a process employ an extraction step in conjunction with the additional chlorination (D) stages. The pulp and the discharge effluents resulting from this prior art extraction option contain higher concentrations of chlorinated organics than are acceptable and/or desirable. Processes using both oxygen delignification and chlorine dioxide substitution have been suggested, but do not achieve the desired concentrations of chlorine-containing residues in either the pulp or the effluent.

In addition, there have been some attempts in the prior art to employ ozone in conjunction with other bleaching agents. For example, Swedish patents SE 467,260 and 467,261, corresponding to Canadian patents 2,031,848 and 2,031,850, respectively, describe a process in which pulp is bleached with chlorine dioxide and ozone in a single stage without an intervening washing stage. However, this reference fails to disclose or suggest the use of other, sequentially applied bleaching agents in the same stage and in conjunction with ozone. U.S. Patent No. 4,959,124 to Tsai discloses a method in which a pulp is initially contacted with chlorine dioxide and then processed through an ozonization stage, without a customary extraction stage. However, this reference teaches that an intervening washing stage between the two bleaching steps is preferred. In

addition, these references do not disclose the use of hypochlorite or chlorine gas in the process; nor is there any suggestion of the bleaching combinations (CDZ), (DCZ), (HDZ), (HCZ), or (DZD). Further, these references do not disclose (APZ), (PAA•Z), (Ca•Z), or (RO•Z).

5 From an environmental perspective, ozone is a superior bleaching agent for cellulosic pulp relative to chlorine and chlorine dioxide. However, ozone alone in a single stage does not provide a pulp of superior brightness, purity and strength, as is obtained with the chlorine agents, C/H/D, sequentially applied prior to ozone treatment. Further, wide use of ozone in pulp bleaching has not been commercially feasible because
10 of the significantly lower selectivity achieved in ozone bleaching. In addition to lignin destruction in the pulp, ozone bleaching also substantially degrades cellulose in the pulp.

The physical characteristics of a pulp can be denoted by means of a number of parameters. The kappa number of a pulp is a measure of the lignin content. The viscosity represents the average chain length of the cellulose and is an indication of its
15 strength. For a bleached pulp of mixed hardwood with a brightness of 90 ISO, the viscosity ought to be above 600 SCAN units (dm^3/kg) to achieve a desired strength.

When a pulp is initially bleached with oxygen and then further bleached with chlorine-based chemicals, four separate steps or stages had been necessary in the prior art to achieve a desired level of brightness, approximately 90 ISO. A partial
20 replacement of total active chlorine with ozone in the first stage will substantially lower AOX, without adversely affecting the pulp properties. Accordingly, there still remains a need in the prior art for a simple, efficient, and effective method of bleaching pulp of cellulosic fibrous material so as to reduce the emission of chlorinated organic compounds.

SUMMARY OF THE INVENTION

25 A primary object of the present invention is to provide an improved method of bleaching pulp of cellulosic fibrous material which considerably reduces adsorbable organic halogen (AOX), but which still employs chlorine by-products from integrated chlorine dioxide generation plants.

Another object of the invention is to provide an improved method of bleaching pulp of cellulosic fibrous material which is more cost-effective relative to conventional bleaching processes.

A further object of the invention is to provide an improved method of
5 bleaching pulp of cellulosic fibrous material which reduces the use of total active chlorine.

A still further object of the invention is to optimize the charges of bleaching agent admixtures, whether based on chlorine-containing chemicals or not.

These objects, among others, have been obtained by a method of bleaching
10 pulp of cellulosic fibrous material in the production of chemical pulp, wherein the pulp, fed continuously through a bleaching line, is bleached with ozone and at least one member of the group of bleaching agents consisting of chlorine dioxide, chlorine, hypochlorite, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides, wherein this bleaching occurs in a single stage and wherein this single stage
15 does not contain an intermediate washing or extraction stage.

In a preferred embodiment of this method, the at least one member of the group of bleaching agents consisting of chlorine dioxide, chlorine, hypochlorite, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides is applied more than once in conjunction with the ozone bleaching. An example of such a sequence is the
20 sequence (DZD).

In a preferred embodiment of the present invention, the method of bleaching pulp of cellulosic fibrous material in the production of chemical pulp is one in which the pulp, fed continuously through a bleaching line, is bleached with ozone and two or more members of the group of bleaching agents consisting of chlorine dioxide,
25 chlorine, hypochlorite, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides, wherein this bleaching occurs in a single stage and wherein this single stage does not contain an intermediate washing or extraction stage.

The ozone and at least one member of the group of bleaching agents are added sequentially. The ozone is normally added last so as to set the redox potential in
30 the reaction vessel. A high shear mixer can be used to ensure sufficient mixing of the

components. Ozone can, however, be followed by chlorine dioxide without an intervening washing stage, for example, the bleaching sequences (DZD), (HZD), and (CZD), among others.

In a preferred embodiment, the present invention comprises a method of
5 bleaching pulp of cellulosic fibrous material in the production of chemical pulp, wherein the pulp, fed continuously through a bleaching line, is bleached with sequential applications of various chlorine-based chemicals and ozone in a single stage and wherein this single stage does not contain an intermediate washing or extraction stage.

In another preferred embodiment, the present invention comprises a
10 method of bleaching pulp of cellulosic fibrous material in the production of chemical pulp, wherein the pulp, fed continuously through a bleaching line, is bleached with a mixture of chlorine and ozone in a single stage and wherein this single stage does not contain an intermediate washing or extraction stage.

In another preferred embodiment, the present invention comprises a
15 method of bleaching pulp of cellulosic fibrous material in the production of chemical pulp, wherein the pulp, fed continuously through a bleaching line, is bleached with sequential applications of various non-chlorine-based bleaching agents from the group of bleaching agents and ozone in a single stage and wherein this single stage does not contain an intermediate washing or extraction stage.

In a still another preferred embodiment of the present invention, this single
20 stage bleaching of the pulp takes place under conditions such that the redox potential of the pulp immediately after the admixture of each bleaching agent is brought down to a level of 0 to about 20 % of the original value of the redox potential prior to the addition of the subsequent bleaching agent.

In a still further preferred embodiment of the present invention, the pH of
25 the pulp remains within the range of about 2 to about 4.

Other preferred embodiments of the present invention include an
embodiment in which the bleaching agent is chlorine or hypochlorite; and one in which
the bleaching agent is a mixture of chlorine and chlorine dioxide. Further preferred
30 embodiments are those in which chlorine is added prior to the addition of ozone; in which

the mixture of chlorine and chlorine dioxide is added prior to the addition of ozone; and in which chlorine and chlorine dioxide are added prior to the addition of ozone.

Another preferred embodiment employs a first chlorine dioxide treatment, subsequent treatment of the pulp with ozone, and a second chlorine dioxide treatment, without any intervening washing or extraction. The second chlorine dioxide treatment can occur either after removal of oxygen and residual ozone (by means of a blowtank) or without an intervening removal of oxygen and residual ozone. This bleaching sequence can be represented as (DZD).

In other embodiments, the pulp is treated with ozone at a pressure in excess of 1 bar overpressure and the bleaching is carried out at a temperature in the range of about 25° C. to about 70° C., more preferably about 45° C. to about 65° C.

The bleaching treatment can be followed by one or two alkali extractions, at least one of which may be reinforced with oxygen gas and/or hydrogen peroxide. These alkali extractions can be performed in sequence with the bleaching treatment without intermediate washing or performed in a separate stage preceded by washing. Subsequently, the pulp can be further bleached with chlorine dioxide or non-chlorine-based bleach chemicals. in one or more stages.

In addition, the bleaching treatment can be followed by one or two chelation steps, preferably employing EDTA. These chelation steps can be performed in sequence with the bleaching treatment without intermediate washing or performed in a separate stage preceded by washing. Subsequently, the pulp can be further bleached with chlorine dioxide in one or more stages.

In addition, the entering pulp can consist of oxygen-delignified pulp which has been cooked continuously.

Other preferred embodiments of the present process include those in which the chlorine or hypochlorite is added in an amount of about 5-20 kg/ADMT, preferably about 5-10 kg/ADMT, calculated as active chlorine; in which the ozone is added in an amount of about 1-5 kg/ADMT, preferably about 2-4 kg/ADMT and in which chlorine dioxide is added for the ultimate bleaching in an amount of about 2-50 kg/ADMT, preferably about 5-20 kg/ADMT, calculated as active chlorine.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same become better understood by reference to the following detailed description when considered in connection with the accompanying drawing, wherein

Figure 1 shows schematically a bleaching plant for carrying out a first embodiment of the present method;

Figure 2 shows schematically a bleaching plant for carrying out a second embodiment of the present method;

Figure 3 diagrams the brightness relative to the ClO_2 charge for four different bleaching processes in the bleaching of mill, oxygen-delignified pulp; and

Figure 4 illustrates the viscosity relative to the brightness for four different bleaching processes in the bleaching of mill, oxygen-delignified pulp.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention comprises a method of bleaching pulp of cellulosic fibrous material in the production of chemical pulp, wherein the pulp, fed continuously through a bleaching line, is bleached with ozone and at least one member of the group of bleaching agents consisting of chlorine dioxide, chlorine, hypochlorite, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides, wherein this bleaching occurs in a single stage and wherein this single stage does not contain an intermediate washing or extraction stage.

In a preferred embodiment of this method, at least one member of the group of bleaching agents consisting of chlorine dioxide, chlorine, hypochlorite, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides can be applied more than once in conjunction with the ozone bleaching.

In another preferred embodiment of the present invention, the method of bleaching pulp of cellulosic fibrous material in the production of chemical pulp is one in which the pulp, fed continuously through a bleaching line, is bleached with ozone and

two or more members of the group of bleaching agents consisting of chlorine dioxide, chlorine, hypochlorite, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides, wherein this bleaching occurs in a single stage and wherein this single stage does not contain an intermediate washing or extraction stage.

5 In addition to the bleaching sequences referred to above, the present process can also include oxidative lignin degradation; suppressed formation of chlorinated lignins; a multichemical oxidative attack on pitch and resins; radical scavenger protection of carbohydrates; a reductive sulfonation stage; and a bleaching process that essentially suppresses chlorination as a result of selection of an appropriate
10 pH and redox potential.

 In an embodiment of the present invention, referring now to Figure 1, pulp of medium consistency (a slurry of about 6-15% pulp) is fed from a supply tank to mixers 50, 51, and 52, where the pulp is treated sequentially with hypochlorite, chlorine dioxide, and ozone, respectively. The treated pulp is then passed to a blow tank 53, where excess
15 oxygen and residual ozone is removed. The pulp is then neutralized with a NaOH solution and passed to a diffuser tower 54, where the pulp is washed.

 Subsequently, the pulp is treated with NaOH, hydrogen peroxide, oxygen, and steam and then passed to a reaction vessel 55, where the pulp undergoes pressurized oxygen treatment. From this stage, the pulp then passes to a wash-press 56 for washing
20 and pressing. After pressing, the pulp then passes to a mixer 57, where chlorine dioxide is again added, and then on to a bleaching tower 58. After washing the pulp in the diffuser, the pulp is then further treated at mixer 59, where chlorine dioxide is again added, and then passed on to bleaching tower 60. After washing pulp in the diffuser, the
25 pulp is treated with caustic and SO₂ for controlling pH and residual active Cl₂ in pulp, prior to passing on to a storage tower.

 The above bleaching process can be described as (HDZE), followed by (EPO)D(ED) bleaching so as to achieve a brightness of 90+ ISO. A similar apparatus can be employed in other bleaching sequences corresponding to the present invention, which include, among others, the bleaching sequences (CDZE), (DCZE), (HCZE), (CHZE),
30 (DZDE), and (DHZE). The neutralization stage E can also be replaced, in another

embodiment, with a D stage. Still further, the D stage can also further comprise a chelate Q so that the sequence (PO)D(ED) can be used for final bleaching. This means that more hydrogen peroxide (5-20 kg of H₂O₂ ptp) can be used in the pressurized peroxide stage. Other embodiments of the bleaching process of the present invention also include, among
5 others, (CZD), (CZP), (DZD), (HZP), and (HZD).

In one example, the pulp is homogeneously mixed in the first mixer with chlorine or chlorine dioxide and is then, after a relatively short period of time when the pH is lowered below, mixed with a carrier gas containing ozone. This brief period of time may be from 10 seconds up to a few minutes, for example, 10 minutes. In a
10 preferred embodiment, 80% up to 100% of the chlorine will have reacted with the pulp before the ozone in gaseous form is added.

Utilizing current technology for the production of ozone, the carrier gas may contain about 10 to 15 per cent by weight ozone. However, with improved methods in the future it may be possible to increase the amount of ozone, for example, up to about
15 20 per cent by weight. The amount of ozone can be controlled by the choice of a suitable gas pressure. Specifically, the higher the gas pressure mixed into the pulp, the more ozone that is mixed in as well. Because the carrier gas is not consumed during the bleaching process, the carrier gas can be recovered, if desired.

If hydrogen peroxide is employed as one of the bleaching agents, a small
20 quantity of oxygen gas may be added to oxidize the easily-oxidized compounds in the pulp, permitting more efficient utilization of the hydrogen peroxide. With hydrogen peroxide, high-pressure steam may also be added in sufficient amount to increase the temperature of the pulp to about 60-90°C.

In an alternate embodiment, ClO₂ can be employed in the bleaching
25 process.

In an alternate embodiment represented in Figure 2, pulp of medium consistency (a slurry of about 6-15% pulp) is fed from the supply tank to mixers 51 and 52, where the pulp is treated sequentially with chlorine dioxide and ozone, respectively. The treated pulp is then passed to a blow tank 53, where excess oxygen and residual

ozone is removed. The pulp is then neutralized with a NaOH solution and passed to a diffuser tower 54, where the pulp is washed.

Subsequently, the pulp is treated with NaOH, hydrogen peroxide, oxygen, and steam and then passed to a reaction vessel 55, where the pulp undergoes pressurized oxygen treatment. From this stage, the pulp then passes to a wash-press 56 for washing and pressing. After pressing, the pulp then passes to a mixer 57, where chlorine dioxide is again added, and then on to a bleaching tower 58. The pulp is then further treated at mixer 59, where chlorine dioxide is again added, and then passed on to bleaching tower 60, where the mixture is extracted with alkali and treated with sulfite, prior to passing on to a storage tower.

This embodiment of the present bleaching process comprises a bleaching sequence with only two bleaching agents, and a washing stage at the conclusion.

Examples of such bleaching processes corresponding to the present invention are (CZ), (ZC), (DZ), and (ZD), among others.

The ozone is added with the aid of a carrier gas containing about 10-13 per cent by weight ozone. The pulp is treated with ozone at a pressure in excess of 1 bar over-pressure, preferably 5-10 bars over-pressure, depending on the ozone charge. The sequence bleaching of pulp with chlorine dioxide and ozone, or alternatively vice versa, is performed at a temperature of 25-70°C, preferably 45-65°C.

The bleaching treatments of the present invention can be followed by one or more alkali extractions, at least one of which may be reinforced with oxygen gas and/or hydrogen peroxide. The first alkali extraction is performed either in sequence with the bleaching treatments without intermediate washing or in a separate stage preceded by washing.

The supplied and treated pulp is preferably of medium consistency, about 6-15%, and suitably consists of oxygen-delignified pulp which has been digested continuously. The pulp may have also been previously treated with ozone.

In another embodiment of the present invention, again referring now to Figure 3, pulp of medium consistency (a slurry of about 6-15% pulp) is fed from a supply tank to mixers 51 and 52, where the pulp is treated sequentially with activated oxygen

(O*) and ozone, respectively. Activated oxygen (O*) includes bleaching agents such as acidic hydrogen peroxide, peracetic acid, persulfuric acid, and organic peroxides. The treated pulp is then passed to a separator 53, where excess oxygen and ozone is removed. The pulp is then neutralized with aqueous NaOH to a pH of about 5 to 6, treated with a
 5 chelating agent like EDTA, and passed to a washing tower 54, where the pulp is washed with white water and alkali.

Subsequently, the pulp is treated in a reductive sulfonation step (R), in which the pulp is treated with bisulfite and chelate. In an exemplary R stage, the pulp is treated with bisulfite and chelate, under neutral to slightly acidic conditions in a
 10 pressurized system for about 0.5 to 2 hours at about 90° to 120° C. and with a final pH of about 2.5 to 5. Such a step combines sulfonation, activation, and chelation in one step.

The treated pulp is then passed to a reaction vessel 55 where the pulp undergoes pressurized oxygen treatment. From this stage, the pulp then passes to a wash
 15 press 56 for washing and pressing. After pressing, the pulp then passes to a mixer 57 where the pulp is treated with a mixture of NaOH and H₂O₂, corresponding to an EOP step, and then on to a bleaching tower 58. The pulp is then further treated at mixer 59, where mixture of NaOH and H₂O₂ is again added, and then passed on to bleaching tower 60, where the mixture is treated with H₂O₂, prior to passing on to a storage tower.

The bleaching process described thus can be illustrated as follows:
 20 [O*(ZQ)](R/EOP)P(PO). The process of the present invention can be also practiced in bleaching processes comprising (DZ)(EO)D(ED); (DZD)(EO)D(ED); (DZD)(EOP)DDP; (DZD)(EO)DDP; [DZ(D+Q)](PO)DDP; [DC(ZE)](EO)DD and [O*(ZQ)](R/EOP)DP.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the
 25 invention and are not intended to be limiting thereof.

Example 1

(DZ)(EO)D(ED) bleaching of mill oxygen-delignified pulp.

Pulp No	12699
Kappa No	8.7
Viscosity, dm ³ /kg	818
Washing loss as COD, kg/BDMT	8.0
Bleach No.	B 3237

(DZ) stage

Consistency, %	10
Temperature, °C	50
Retention time between D and Z, sec	40
Charge H ₂ SO ₄ kg/BDMT	7.0
Charge O ₃ , kg/BDMT	3.0
Charge active chlorine, kg/BDMT	13
End pH	2.9
Kappa No.	3.3

(Before wash the pulp was neutralized to pH 6.0 during 1 hour at 50°C)

(EO) stage

Consistency, %	10
Temperature, °C	100
Time, min	60
Average pressure, bar (excess)	5.0
Charge MgSO ₄ kg/BDMT	3.0
Charge NaOH, kg/BDMT	20
End pH	11.3
Kappa No.	2.0
Viscosity, dm ³ /kg	621

D1 (chlorine dioxide)

Consistency, %	10		
Temperature, °C	75		
Time, min	180		
Charge active chlorine, kg/BDMT	10	20	30
Residual active chlorine, kg/BDMT	-	-	0.9
End pH	4.5	4.5	4.5
Brightness, % ISO	82.7	87.2	87.9
Viscosity, dm ³ /kg	607	601	590

E2. Extraction

Consistency, %	10
Temperature, °C	75
Time, min	5
Charge NaOH, kg/BDMT	2
	no wash

D2 (chlorine dioxide)

Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	10	10	10
Residual active chlorine, kg/BDMT	0.6	0.9	0.6
End pH	4.6	4.6	4.6
Brightness, % ISO	87.9	89.2	89.6
Rev brightness, % ISO	86.1	87.6	87.9
Viscosity, dm ³ /kg	599	593	581
Charge ozone, kg/ADMT bleached pulp	3	3	3

Charge active chlorine, kg/ADMTbleached pulp

ClO ₂ in (DZ)	12	12	12
ClO ₂ in D1 stage	9.2	18.4	27.6
ClO ₂ in D2 stage	9.2	9.2	9.2
ClO ₂ total	30	40	49

Example 2

(DZ)(EO)D(ED) bleaching of mill oxygen-delignified pulp.

5

Pulp No	12699
Kappa No.	8.7
Viscosity, dm ³ /kg	818
Washing loss as COD, kg/BDMT	8.0
Bleach No	B 3238

(DZ) stage

Consistency, %	10
Temperature, °C	50
Retention time between D and Z, sec	40
Charge H ₂ SO ₄ , kg/BDMT	7.0
Charge O ₃ , kg/BDMT	4.0
Charge active chlorine, kg/BDMT	13
End pH	3.0
Kappa No.	2.8
(Before wash the pulp was neutralized to pH 6.0 during 1 hour at 50°C)	

<u>(EO) stage</u>			
Consistency, %		10	
Temperature, °C		100	
Time, min		60	
Average pressure, bar (excess)		5.0	
Charge MgSO ₄ kg/BDMT		3.0	
Charge NaOH, kg/BDMT		20	
End pH		11.1	
Kappa No		1.6	
Viscosity, dm ³ /kg		590	
<u>D1 (chlorine dioxide)</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	10	20	30
Residual active chlorine, kg/BDMT	-	-	0.9
End pH	4.5	4.5	4.5
Brightness, % ISO	86.1	88.7	89.3
Viscosity, dm ³ /kg	579	569	564
<u>E2, Extraction</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		5	
Charge NaOH, kg/BDMT		2	
		no wash	
<u>D2 (chlorine dioxide)</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	10	10	10
Residual active chlorine, kg/BDMT	0.6	0.6	0.6
End pH	4.6	4.6	4.6
Brightness, % ISO	89.3	90.0	90.1
Rev. brightness, % ISO	87.6	88.6	88.7
Viscosity, dm ³ /kg	572	562	543
Charge ozone, kg/ADMT bleached pulp	4	4	4
<u>Charge active chlorine, kg/ADMT</u>			
<u>bleached pulp</u>			
ClO ₂ in (DZ)	12	12	12
ClO ₂ in D1 stage	9.2	18.4	27.6
ClO ₂ in D2 stage	9.2	9.2	9.2
ClO ₂ total	30	40	48

Example 3

(DZD)(EO)D(ED) bleaching of mill oxygen-delignified pulp.

Pulp No	12699
Kappa No.	8.7
Viscosity, dm ³ /kg	818
Washing loss as COD, kg/BDMT	8.0
Bleach No	B 3240

(DZD) stage

Consistency, %	10
Temperature, °C	50
Retention time between D and Z, sec	40
Charge H ₂ SO ₄ , kg/BDMT	7.0
Charge O ₃ , kg/BDMT	2.0
Charge active chlorine, kg/BDMT	10+10
End pH	2.9
Kappa No.	3.3

(EO) stage

Consistency, %	10
Temperature, °C	100
Time, min	60
Average pressure, bar (excess)	5.0
Charge MgSO ₄ kg/BDMT	3.0
Charge NaOH, kg/BDMT	20
End pH	11.1
Kappa No	1.8
Viscosity, dm ³ /kg	682

D1 (chlorine dioxide)

Consistency, %	10		
Temperature, °C	75		
Time, min	180		
Charge active chlorine, kg/BDMT	10	20	30
Residual active chlorine, kg/BDMT	-	-	1.2
End pH	4.5	4.5	4.5
Brightness, % ISO	86.0	88.4	89.3
Viscosity, dm ³ /kg	665	660	645

E2, Extraction

Consistency, %	10
Temperature, °C	75
Time min	5
Charge NaOH, kg/BDMT	2

		no wash	
<u>D2 (chlorine dioxide)</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	10	10	10
Residual active chlorine, kg/BDMT	0.8	0.9	0.9
End pH	4.6	4.5	4.6
Brightness, % ISO	89.1	89.9	90.4
Rev. brightness, % ISO	87.1	88.4	88.7
Viscosity, dm ³ /kg	652	641	618
Charge ozone, kg/ADMT bleached pulp	2	2	2
<u>Charge active chlorine, kg/ADMT bleached pulp</u>			
ClO ₂ in (DZD)	18.4	18.4	18.4
ClO ₂ in D1 stage	9.2	18.4	27.6
ClO ₂ in D2 stage	9.2	9.2	9.2
ClO ₂ total	37	46	55

Example 4

(DZD)(EOP)D(ED)P bleaching of mill oxygen-delignified pulp.

Pulp No	12699
Kappa No.	8.7
Viscosity, dm ³ /kg	818
Washing loss as COD, kg/BDMT	8.0
Bleach No	B 3248

(DZD) stage

Consistency, %	10
Temperature, °C	50
Retention time between D and Z, sec	40
Retention time second D stage, min	45
Charge H ₂ SO ₄ , kg/BDMT	7.0
Charge O ₃ , kg/BDMT	4.0
Charge active chlorine, kg/BDMT	10+15
Residual active chlorine, kg/BDMT	0
End pH	2.4
Kappa No.	1.9

<u>(EOP) stage</u>			
Consistency, %		10	
Temperature, °C		100	
Time, min		60	
Average pressure, bar (excess)		5.0	
Charge MgSO ₄ , kg/BDMT		3.0	
Charge NaOH, kg/BDMT		20	
Charge H ₂ O ₂ , kg/BDMT		3.0	
End pH		10.9	
Kappa No		0.9	
Viscosity, dm ³ /kg		641	
<u>D1 (chlorine dioxide)</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	20	30	40
Residual active chlorine, kg/BDMT	1.9	2.0	3.7
End pH	4.1	3.9	2.8
Brightness, % ISO	89.0	89.3	89.0
Viscosity, dm ³ /kg			
<u>E2. Extraction</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		5	
Charge NaOH, kg/BDMT		2	
		no wash	
<u>D2 (chlorine dioxide)</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	10	10	10
Residual active chlorine, kg/BDMT	1.0	1.4	1.6
End pH	4.6	4.6	4.5
Brightness, % ISO	90.4	90.6	90.6
Rev. brightness, % ISO			
Viscosity, dm ³ /kg			

<u>P stage</u>			
Consistency, %		10	
Temperature, °C		70	
Time, min		120	
Charge NaOH, kg/BDMT		2	
Charge H ₂ O ₂ , kg/BDMT		2	
End pH	10.5	10.4	10.3
Brightness, % ISO	90.8	91.2	91.2
Rev. brightness, % ISO			
Viscosity, dm ³ /kg			
Charge ozone, kg/ADMT bleached pulp	4	4	4
Charge peroxide, kg/ADMT bleached pulp	5	5	5
<u>Charge active chlorine, kg/ADMT bleached pulp</u>			
ClO ₂ in (DZD)	23	23	23
ClO ₂ in D1 stage	18.4	27.6	36.8
ClO ₂ in D2 stage	9.2	9.2	9.2
ClO ₂ total	51	60	69

Comparative Example

(D)(EO)D(ED) bleaching of mill oxygen-delignified pulp.

5

Pulp No.	12699
Kappa No	8.7
Viscosity, dm ³ /kg	818
Washing loss as COD, kg/BDMT	8.0
Bleach No	B 3236

<u>D stage</u>	
Consistency, %	10
Temperature, °C	50
Time, sec	30
Multiple kg active chlorine/BDMT/kappa No	2.4
Charge active chlorine, kg/BDMT	20.9
Residual active chlorine, kg/BDMT	0
End pH	2.0

<u>(EO) stage</u>			
Consistency, %		10	
Temperature, °C		100	
Time, min		60	
Average pressure, bar (excess)		5.0	
Charge MgSO ₄ , kg/BDMT		3.0	
Charge NaOH, kg/BDMT		20	
End pH		11.1	
Kappa No		1.9	
Viscosity, dm ³ /kg		756	
<u>D1 (chlorine dioxide)</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	10	20	30
Residual active chlorine, kg/BDMT	-	-	1.7
End pH	4.5	4.4	4.3
Brightness, % ISO	85.4	87.3	87.9
Viscosity, dm ³ /kg	741	730	721
<u>E2. Extraction</u>			
Consistency, %		10	
Temperature °C		75	
Time, min		5	
Charge NaOH, kg/BDMT		2	
		no wash	
<u>D2 (chlorine dioxide)</u>			
Consistency, %		10	
Temperature, °C		75	
Time, min		180	
Charge active chlorine, kg/BDMT	10	10	10
Residual active-chlorine, kg/BDMT	0	0.3	0.8
End pH	4.7	4.7	4.7
Brightness, % ISO	88.7	89.3	89.7
Rev. brightness, % ISO	87.0	87.8	87.9
Viscosity, dm ³ /kg	714	705	684
<u>Charge active chlorine, kg/ADMT</u>			
<u>bleached pulp</u>			
ClO ₂ in D	19.2	19.2	19.2
ClO ₂ D1 stage	9.2	18.4	27.6
ClO ₂ in D2 stage	9.2	9.2	9.2
ClO ₂ total	38	47	56

The results regarding brightness, in % ISO, relative to the charge of ClO_2 as active chlorine, expressed as kg/ADMT, for Examples 1, 2, and 3 and the Comparative Example are presented in Figure 3. The results regarding viscosity, in dm^3/kg , relative to brightness, in % ISO, for Examples 1, 2, and 3 and the Comparative Example are
5 presented in Figure 4. These two figures, as well as the data in the tables, demonstrate that the bleaching sequences of the present invention provide superior selectivity and consumption of bleach chemicals. Specifically, these bleach tests indicate the bleaching sequence (DZD)(EO)DD of the present invention provided a brightness of 90-91 ISO at SCAN viscosity $620 \text{ dm}^3/\text{kg}$ on mill pulp. In contrast, the bleaching sequence D(EO)DD
10 of the prior art did not reach a target of 90 ISO, despite excessive use of ClO_2 .

The combined use of ozone and chlorine dioxide permits bleaching to 90-91 ISO without elemental chlorine. To achieve brightness values of 92+ISO, hydrogen peroxide can also be included, as in the bleaching sequence (DZD)(EOP)DDP. The final peroxide stage is carried out at atmospheric pressure and can take place in an available
15 storage tank. The sequence [DZ(D+Q)] (PO) DDP with DTPA chelant using pressurized peroxide, also a bleaching sequence of the present invention, would be even more powerful.

The bleaching sequence (DZD)(EO)DD of the present invention provides adequate and sufficient charge of ClO_2 in the first stage, as well as enabling prestages
20 such as (HZD), (DZ), (ZD), Z or D in the same bleaching line. Pulps approaching ECF pulps, with an AOX < 0.5 - 0.6 kg ptp, can thus be produced using hypochlorite from Cl_2 .

The bleaching sequence of the present invention provides many advantages and benefits relative to the prior art. The use of ozone in the present pulp bleaching sequence results in lowered process costs, because the amount of chlorine employed in
25 the bleaching process is reduced relative to conventional processes. Further, the use of the bleaching agents in a single stage, without an intervening washing or extracting stage, also reduces process costs.

Additionally, the use of ozone in the pulp bleaching process provides a significant improvement in pulp quality. The bleached yield of pulp from the present
30 process is about 0.2 to 0.3 % higher than the conventional processes. Further, the

viscosity of the pulp is improved by 20 to 40 SCAN units relative to pulps produced by the processes of the prior art. The present bleaching process also results in superior beatability; there is a 10 to 20% lowering in the beating energy requirement with the pulp of the present invention relative to that of the prior art. The pulp of the present process
5 also has a 15% greater tear strength. Still further, the present pulp possesses a lower resin and speck content; reduced AOX; and decreased dioxin content.

Additionally, the pulp of the present process significantly reduces the impact of the bleaching process on the environment. The present process yields a pulp with a greatly lowered content of chlorinated organics, having an AOX of 0.2 to 0.4
10 kilograms per ton of pulp. Further, the pulp has a significantly lower COD (chemical oxygen demand) content - 10 to 20% relative to conventional pulps. There is a reduction in the amount of chlorine gas employed in the present process. Moreover, the effluent from the present process is environmentally more benign than those of conventional processes, in that it is essentially free of chlorine and permits a gradual move in the future
15 to a bleaching process that is totally free of chlorine. Moreover, the present process will permit compliance with the stricter environmental regulations regarding chlorine anticipated in the near future.

An analysis of the savings in process costs indicates that the present process results in a savings of approximately \$20 (US) per ton of pulp, in which about \$8
20 is achieved through savings in chemical costs, essentially chlorine dioxide and hydrogen peroxide; about \$2 in improved yield of pulp; and about \$10 in added product value. Such costs translate into a savings of \$10,000,000 per year for a typical pulp mill producing 1500 tons of pulp per day. Still further, the present process offers the possibility of an inexpensive retrofit of existing pulp equipment so as to achieve the
25 enhanced, improved pulp production attained with the present process.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

THAT WHICH IS CLAIMED IS:

- 1 1. A method of bleaching cellulosic kraft pulp, comprising the steps of
2 feeding the pulp continuously through a bleaching line and
3 bleaching the pulp with ozone and at least one bleaching agent selected
4 form the group consisting of chlorine dioxide, hypochlorite, chlorine, acidic hydrogen
5 peroxide, peracetic acid, persulfuric acid, and organic peroxides, in a single stage,
6 wherein said single stage is free from an intermediate washing or extraction step.
- 1 2. The method according to Claim 1, wherein said at least one bleaching
2 agent is chlorine.
- 1 3. The method according to Claim 1, wherein said at least one bleaching
2 agent is a mixture of chlorine and chlorine dioxide.
- 1 4. The method according to Claim 1, wherein said at least one bleaching
2 agent are chlorine and chlorine dioxide.
- 1 5. The method according to Claim 2, wherein said chlorine is added prior to
2 the addition of ozone.
- 1 6. The method according to Claim 3, wherein said mixture of chlorine and
2 chlorine dioxide is added prior to the addition of ozone.
- 1 7. The method according to Claim 3, wherein said chlorine and chlorine
2 dioxide are added prior to the addition of ozone.
- 1 8. The method according to Claim 1, wherein the redox potential of the pulp
2 immediately after the addition of each bleaching agent is within a value of 0 to about 20%
3 of the redox potential prior to the addition of the subsequent bleaching agent.

1 9. The method according to Claim 1, wherein the pH of the pulp after said
2 bleaching is within the range of about 2 to about 5.5.

1 10. The method according to Claim 1, wherein the pH of the pulp after said
2 bleaching is within the range of about 2.5 to about 3.5.

1 11. The method according to Claim 1, wherein the pulp is treated with ozone at
2 a pressure in excess of 1 bar overpressure.

1 12. The method according to Claim 1, wherein said bleaching is performed at a
2 temperature of about 25-70° C.

1 13. The method according to Claim 12, wherein said bleaching is performed at
2 a temperature of about 45-65° C.

1 14. The method according to Claim 1, wherein said bleaching is followed by at
2 least one alkali extraction, which may be reinforced with at least one member selected
3 from the group consisting of oxygen gas and hydrogen peroxide.

1 15. The method according to Claim 14, wherein said at least one alkali
2 extraction is performed in sequence with said bleaching without intermediate washing.

1 16. The method according to Claim 15, wherein said at least one alkali
2 extraction is performed in a separate stage preceded by washing.

1 17. The method according to Claim 1, wherein said bleaching is followed by at
2 least one chelation step.

1 18. The method according to Claim 17, wherein said at least one chelation step
2 is performed in sequence with said bleaching without intermediate washing.

1 19. The method according to Claim 17, wherein said at least one chelation step
2 is performed in a separate stage preceded by washing.

1 20. The method according to Claim 1, wherein the pulp is further bleached
2 with chlorine dioxide in one or more stages.

1 21. The method according to Claim 1, wherein the entering pulp consists of
2 oxygen-delignified pulp which has been cooked continuously.

1 22. The method according to Claim 1, wherein the chlorine dioxide is added in
2 an amount of about 1-20 kg/ADMT.

 23. The method according to Claim 19, wherein the chlorine dioxide is added
in an amount of about 1-10 kg/ADMT.

1 24. The method according to Claim 1, wherein the ozone is added in an
2 amount of about 1-10 kg/ADMT.

1 25. The method according to Claim 21, wherein the ozone is added in an
2 amount of about 1-5 kg/ADMT.

1 26. The method according to Claim 17, wherein chlorine dioxide is added in
2 further bleaching in an amount of about 10-50 kg/ADMT.

1 27. The method according to Claim 22, wherein chlorine dioxide is added in
2 further bleaching in an amount of about 10-30 kg/ADMT.

1 28. The method according to Claim 1, wherein said at least one bleaching
2 agent comprises at least two bleaching agents selected from the group consisting of

3 chlorine dioxide, chlorine, acidic hydrogen peroxide, peracetic acid, persulfuric acid, and
4 organic peroxides.

1 29. The method according to Claim 28, wherein said at least two bleaching
2 agents are a mixture of chlorine and chlorine dioxide.

1 30. The method according to Claim 28, wherein said at least two bleaching
2 agents are chlorine and chlorine dioxide.

1 31. The method according to Claim 29, wherein said chlorine is added prior to
2 the addition of ozone.

1 32. The method according to Claim 29, wherein said mixture of chlorine and
2 chlorine dioxide is added prior to the addition of ozone.

1 33. The method according to Claim 30, wherein said chlorine and chlorine
2 dioxide are added prior to the addition of ozone.

1 34. The method according to Claim 28, wherein said bleaching is followed by
2 at least one alkali extraction, which may be reinforced with at least one member selected
3 from the group consisting of oxygen gas and hydrogen peroxide.

1 35. The method according to Claim 34, wherein said at least one alkali
2 extraction is performed in sequence with said bleaching without intermediate washing.

1 36. The method according to Claim 35, wherein said at least one alkali
2 extraction is performed in a separate stage preceded by washing.

1 37. The method according to Claim 28, wherein said bleaching is followed by
2 at least one chelation step.

1 38. The method according to Claim 37, wherein said at least one chelation step
2 is performed in sequence with said bleaching without intermediate washing.

1 39. The method according to Claim 37, wherein said at least one chelation step
2 is performed in a separate stage preceded by washing.

1 40. The method according to Claim 28, wherein the pulp is further bleached
2 with chlorine dioxide in one or more stages.

1 41. The method according to Claim 28, wherein the entering pulp consists of
2 oxygen-delignified pulp which has been cooked continuously.

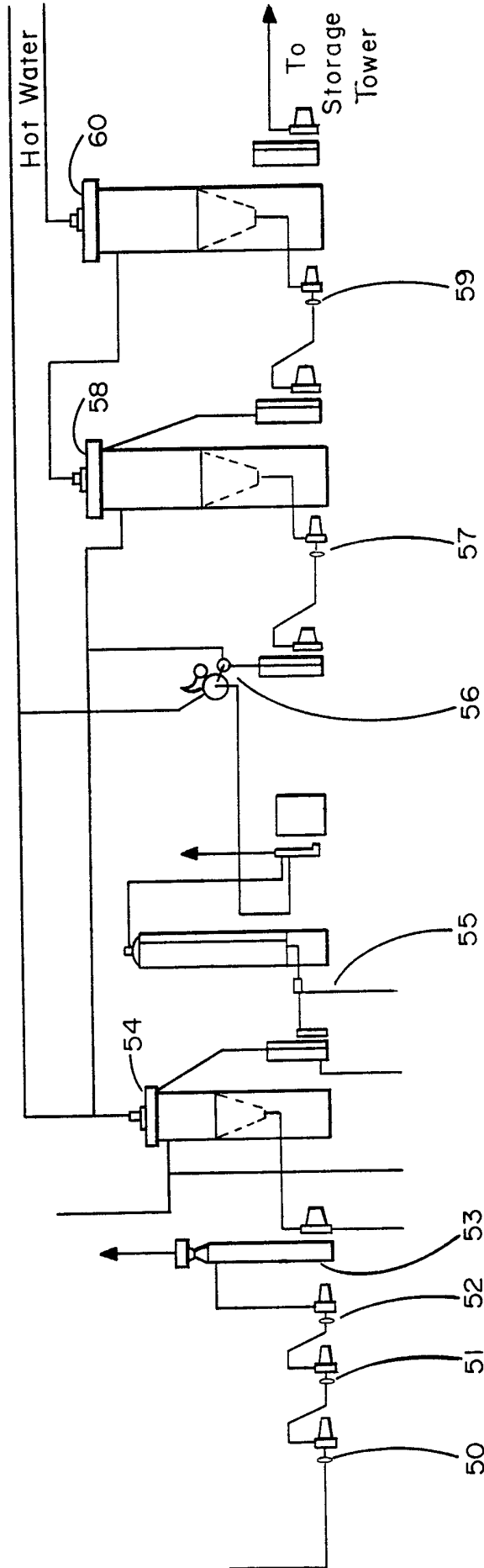


FIG. 1

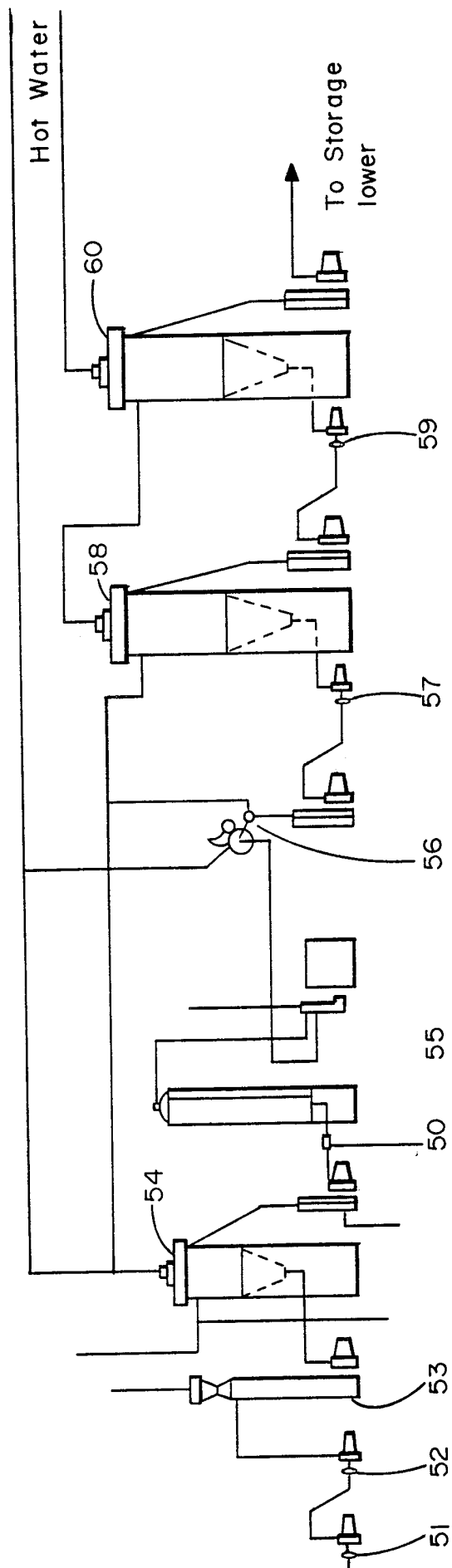


FIG. 2

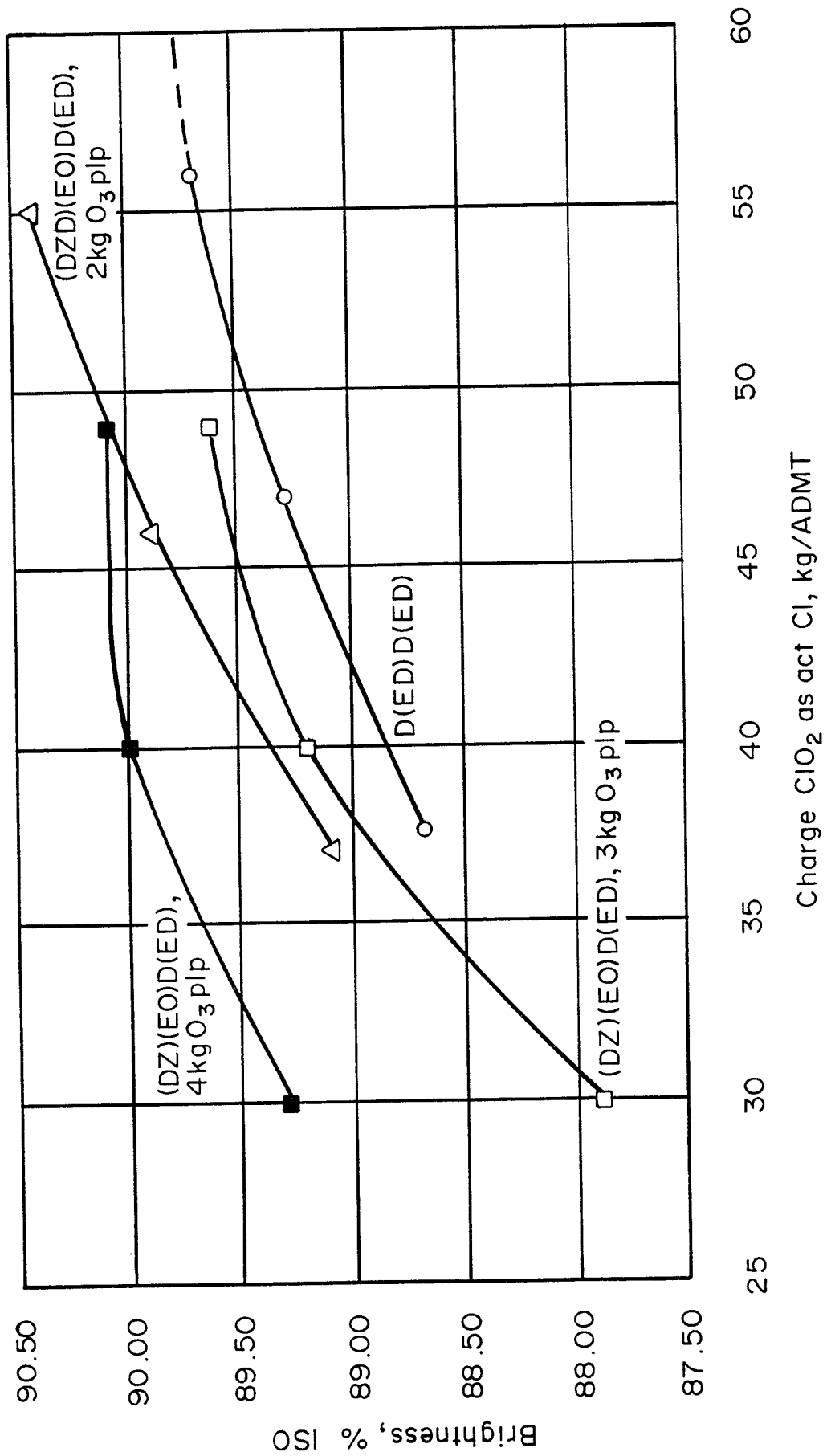
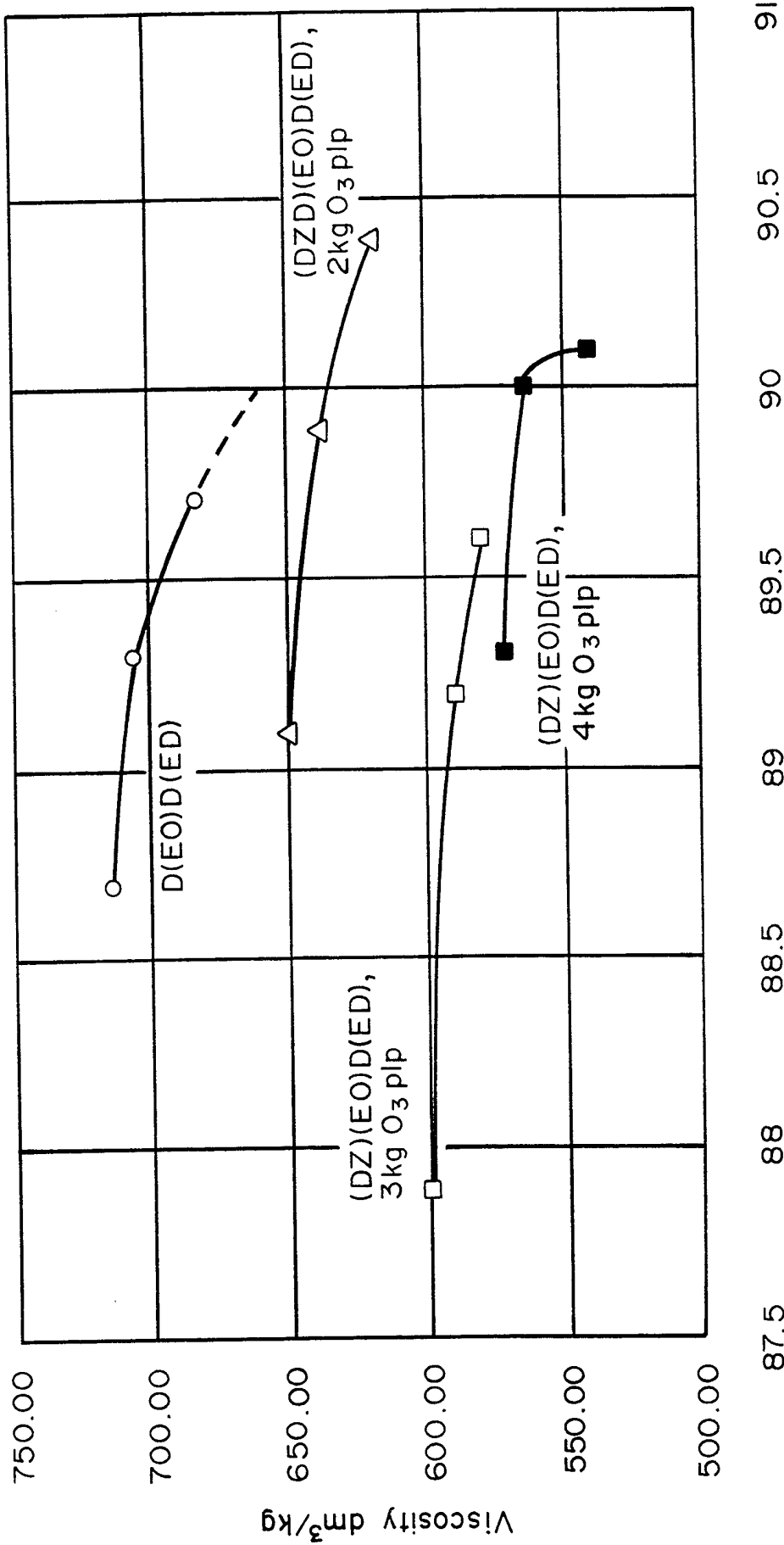


FIG. 3



Brightness, % ISO

FIG. 4

INTERNATIONAL SEARCH REPORT

In national Application No
PCT/IB 98/01318

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21C9/153 D21C9/14 D21C9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 92 17639 A (INT PAPER CO) 15 October 1992 see the whole document ---	1-7, 9-16, 20-36, 40, 41
X	FR 2 663 348 A (CENTRE TECH IND PAPIER) 20 December 1991 see the whole document ---	1, 3, 4, 6, 7, 9-12, 14, 16, 21-25, 28-34, 36, 41
-/--		

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

10 March 1999

Date of mailing of the international search report

16/03/1999

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 98/01318

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 743 094 A (CENTRE TECH IND PAPIER) 4 July 1997 see page 1 - page 3; claims; examples 1,2,5 -----	1,3,4,6, 7,9-12, 14,16, 21-25, 28-34, 36,41
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In. nal Application No

PCT/IB 98/01318

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