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71 Applicant: **AIR PRODUCTS AND CHEMICALS, INC.**
7201 Hamilton Boulevard
Allentown, PA 18195-1501(US)

72 Inventor: **Dalton, Augustine Ivanhoe**
2430 River Rock Road
Macungie, PA 18062(US)

74 Representative: **Kador & Partner**
Corneliusstrasse 15
W-8000 München 5(DE)

54 **Delignification of lignocellulose-containing fiber.**

57 Reduction in required amounts of chlorine and optionally chlorine dioxide in the chlorination stage (C or C_D) of a multi stage process for delignification and bleaching of lignocellulosic pulp is achieved by increasing the temperature and O₂ normally employed in the oxygen alkali extraction stage (E_o) concurrently with the addition of hydrogen peroxide to the pulp just before or after introduction of the molecular oxygen used in the oxygen alkali extraction stage.

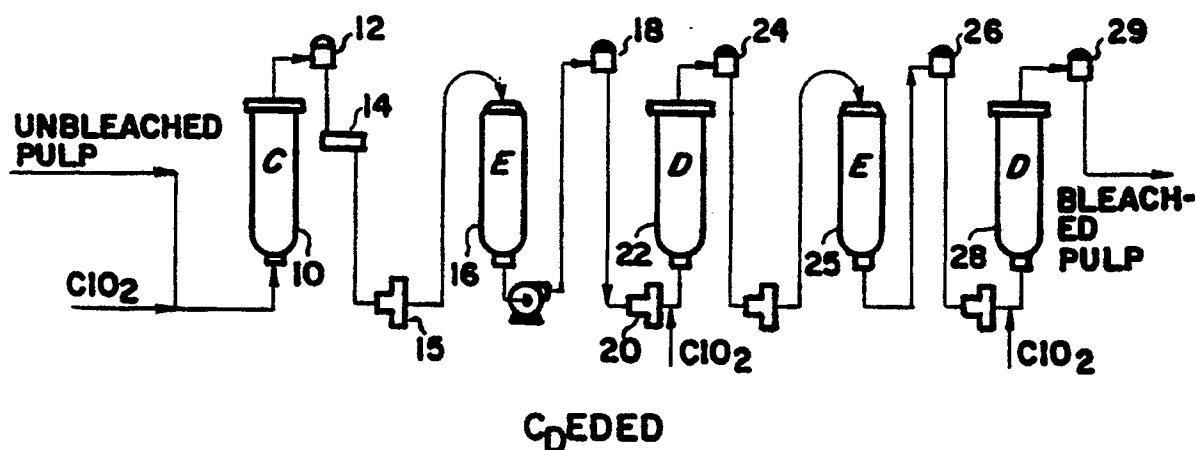


FIG. 1

DELIGNIFICATION OF LIGNOCELLULOSE-CONTAINING FIBER

TECHNICAL FIELD

The present invention is directed to improvements in processes for bleaching and delignification of wood pulp and other lignocellulosic material.

BACKGROUND OF THE INVENTION

In the production of bleached pulp, unbleached brown pulp ("brown-stock") from the pulp mill is directed to the bleach plant where it is subjected to a sequential series of alternating delignifying/bleaching and extraction steps, each stage involving distinctively different bleaching chemicals and/or process conditions. Whereas the process objective of pulping is to chemically delignify wood or other lignocellulosic material (remove the lignin "glue" that binds the cellulosic fibers together), the primary objective of bleaching is to whiten the pulp, albeit some residual delignification occurs. In pulping, the measure of effectiveness is the content of the remaining lignin and lignin residues, which is commonly expressed as the Kappa or permanganate number. In bleaching, one still determines the Kappa number, but the primary analytical parameters are the pulp brightness and viscosity.

Essentially, all commercially practiced bleach processes are chlorine-based. A variety of sequences are used to bleach pulp to the desired target brightness levels, typically greater than 79 brightness units (ISO) and commonly 84-88. The latter stages tend to involve milder, and more selective, and correspondingly more expensive bleaching agents like ClO_2 . The more common bleach sequences use molecular chlorine, chlorine dioxide, or hypochlorite. Among the more common bleach sequences are CEDED, OCE_0D , CE_0D , CEDE_pD , CEHD, and CE_0HD with the first alkaline extraction stage (E) commonly reinforced with oxygen (E_0); where:

C = Chlorination with chlorine (Cl_2), commonly accomplished with co-addition (C_0) or pretreatment (D/C) with chlorine dioxide.

E = Alkali Extraction with NaOH.

E_p or E_0 = Peroxide or oxygen-reinforced alkali extraction.

D = Dioxide treatment with chlorine dioxide (ClO_2).

H = Alkaline Hypochlorite bleaching, typically with sodium hypochlorite (NaOCl).

O - Oxygen bleaching with molecular oxygen (O_2).

The actual sequence utilized by a given plant is a reflection not only of target brightness, but also local process economics, brownstock species, end use of pulps, and age of the bleach plant.

Concern over the negative impact on the environment of chlorine-based bleach plant effluents has accelerated in recent years particularly since the discovery of the highly toxic chlorinated dioxins and furans in some bleach plant effluents, sludge, and pulp products. Today it is generally accepted that it is critical to reduce the amount of chloro-organics in pulp and the plant effluent.

Formation of these chlorinated organics is strongly related to the use and consumption level of molecular chlorine in the chlorination stage (Axegard, P., 1988 Pulping Conference, page 307). Reduced Cl_2 dosage results in reduced organochlorides, commonly referred to collectively as TOC/AOX. However, in the absence of alternative technology, the required Cl_2 dosage cannot be arbitrarily reduced without significant adverse effect on pulp quality. It is of great importance to minimize formation of chloro-organics through identifying a cost-effective means allowing a reduction in the required amount of molecular chlorine utilized in the chlorination stage, rather than rely on post-treatment technologies such as advanced wastewater treatment systems for the effluent.

The dominant cost items in the production of bleached pulps are chemical costs and investment/capital costs, the latter due mainly to the number of chemical treating stages involved. Accordingly any acceptable technology desirably would build on existing process technology and be sensitive to capital requirements and chemical costs. Ideally the technology would use existing onsite chemicals and equipment.

The two most accepted technologies for reduction in the required molecular chlorine are oxygen pretreatment and partial substitution of chlorine with chlorine dioxide in the chlorination stage. Both are being commercially implemented (L. Tench and S. Harper, TAPPI 55 (1987); G. E. Annergren, et al., Svensk Papperstripping, 90, 29 (1987). Oxygen bleaching preceding chlorination can reduce chlorine requirements up to 45% before pulp strength properties are adversely affected. Significant chemical cost savings are also

realized. However, payback is very long due to the huge capital investment in the oxygen prebleach stage (e.g., CEDED → OCEDED) and additional plant retrofit requirements such as additional washers or new recovery boilers to accept the added non-chlorine containing load from the oxygen stage.

Chlorine reduction can also be achieved by substituting part of the chlorine requirements by high levels of chlorine dioxide in the chlorination stage. Although not as common as oxygen prebleaching, the chief advantage is that theoretically no significant capital is involved. However most mills do not have sufficient ClO₂ capacity to handle the additional load. Although one achieves the environmental objective of reduced chlorine consumption, the chemical savings advantage of oxygen bleaching is lost since one is substituting the considerably more expensive chlorine dioxide

(45-50¢/lb)

for chlorine

(8-10¢/lb).

Also, the increased consumption of chlorine dioxide may require investment in additional on-site dioxide generators since the dioxide is unstable and must be made on-site as needed. Furthermore, dioxide substitution technology is not as effective in "short sequence" bleach processes arising from oxygen alkali extraction (E₀) technology when high brightness pulps are required (Annergren, G. E., et al., 1988 INTERNATIONAL PULP BLEACHING CONFERENCE PROCEEDINGS, pp. 37-46).

Oxygen-reinforced alkali extraction (E₀), is now commonly practiced in most bleach plants. E₀ is a relatively low capital, chemical cost-savings technology that simply involves mixing/injecting oxygen into the alkaline pulp of the first alkaline extraction stage which results in reduced chemical requirements in the subsequent bleach stages. The reduced chemical requirement to achieve brightness often allows the option of converting a five stage bleach processes to only three stages ("short sequence bleaching"); e.g., C₀ED₀ED → C₀E₀D (J. S. Enz, et al., TAPPI, 143 (1984) at optimal conditions of 60 °C and 25 psig, an O₂ contact time of no more than 5 minutes is required, and these systems are so designed. Higher pressures and longer reaction times are of no benefit (B. Van Lierop, et al., TAPPI 75, December 1986); nor are they available in existing E₀ processes. Similarly, there is no advantage to increase temperature above 50 °C (B. Van Lierop, et al., Proceedings 1985 International Pulp Bleaching Conference, 83); the E₀ process is run at 50-70 °C because that was the prior existing E-stage temperature. Added reinforcement chemicals such as hypochlorite (E_{0/H}) or peroxide (E_{0/P}) can also be beneficial to incrementally attaining higher brightness pulps or further reducing chemical consumption in the post-E₀ bleach stages, (Nonni, U.S. Patent 4,568,420 (1986)).

E₀ technology is optimized for and directed to saving bleach chemicals in the subsequent (3rd stage and later) stages. Recently it was reported by Sjoblom, et al. (K. Sjoblom, et al., 1988 Int'l Pulp Bleaching Conference, pages 263-270) that a chlorine reduction in the chlorination stage could be achieved by increasing the dosage of the very expensive chlorine dioxide to the chlorination stage as previously disclosed by Annergren, et al., (1988 Int'l Pulp Bleaching Conference, page 37) and also modifying the E₀ stage conditions including increased temperature, pressure, oxygen contact time, added MgSO₄ and optionally reinforcing the E₀ stage with hydrogen peroxide. Pulp brightness could be maintained only with increased chlorine dioxide dosages to the chlorination stage which was disclosed by Annergren, et al. 1988 Int'l Pulp Bleaching Conference, page 37, and also by Axegard (TAPPI Journal, 54, October 1986). Even so, the utility of the described process is severely limited. To reduce required chlorine by this technology, an increase in bleach chemical costs is required as well as additional reinvestment in new E₀ process equipment to accommodate the required increased O₂ reaction times and additional chlorine dioxide capacity. To reduce relatively inexpensive chlorine, as therein proposed, one must incur the costs of the considerably more expensive chlorine dioxide, hydrogen peroxide, MgSO₄ and added capital equipment.

The vast majority of E₀ systems are of the upflow-downflow configuration and are sized for a 3-5 minute reaction time at 25 psig. (B. VanLierop, et al., TAPPI 75, December 1986). The proposed "hot extraction" technology (K. Sjoblom, et al., op. cit.) requires greater pressures and considerably longer oxygen contact reaction times approaching 30-40 minutes. Only in a system providing an upflow E₀ stage, which is relatively uncommon, is sufficient residence time available to accommodate the technology without a major reinvestment in new E₀ process equipment, as well as additional ClO₂ capacity.

In summary, all approaches to significantly reduce the required amount of chlorine require investment in significant new capital equipment or in additional and expensive bleaching chemicals.

Among the objects of the present invention is to provide an improved bleaching process comprising a simple and easily implemented chlorine-reduction technology that does not simultaneously require significant capital investment and which results in net chemical savings while achieving desired pulp brightness and strength (viscosity).

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SUMMARY OF THE INVENTION

In accordance with the present invention the required dosage/charge of chlorine and/or both chlorine and chlorine dioxide is reduced without detriment to final brightness and viscosity, by heating the pulp to 85-100° C and addition of a small amount of hydrogen peroxide to the pulp (without need of magnesium sulfate or other stabilizer) just prior to or directly after the addition of oxygen in the existing E₀ stage. The process of the invention is applicable to treatment of lignocellulosic pulp in a multistage bleaching process comprising sequential chlorination and oxygen alkali extraction stages in which the chlorination stage optionally contains either or both chlorine (Cl₂) and/or chlorine dioxide (ClO₂), conventionally indicated as a C, C_D or D/C stage.

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BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more clearly understood and its several advantages appreciated from the description which follows read in connection with the accompanying drawings, wherein:

Figure 1 is a schematic flow diagram of a conventional 5 step multistage ing chlorination (C).

Figure 2 is a schematic flow diagram of a modified bleaching system employing only 3 treating stages, having an oxygen reinforced alkali extraction stage (E₀), that may be employed in practice of an exemplary embodiment of the present invention.

Figure 3 is a graphic representation of experimental data demonstrating loss of pulp brightness observed as a result of arbitrarily reducing chlorine charge in the initial chlorination stage of a short bleach sequence (C_DE₀D).

Figure 4 is a series of bar graphs demonstrating loss of brightness with reduced Cl₂ even at various E₀ reinforcement conditions based on data recorded in Examples 1 through 6.

Figure 5 is a series of bar graphs of experimental data demonstrating final brightness can be maintained at reduced Cl₂ dosage only by increasing temperature and addition of peroxide before excess oxygen introduction into underchlorinated pulp (Examples 7 and 8) as compared to control (conventional) conditions (Examples 1 and 2).

Figure 6 is a graphic representation of experimental data demonstrating effect of modified E₀ stage conditions on final pulp brightness of underchlorinated pulp in a short sequence (C_DE₀D), comparing Example 12 with a control under conventional Cl₂ and E₀ conditions (Example 9).

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DETAILED DESCRIPTION

Figure 1 illustrates an embodiment of a conventional system employing a five-stage sequence for delignification and bleaching of wood pulp. The illustrated system comprises 5 consecutive treating towers designated C (chlorination), E (alkali extraction), D (ClO₂ treatment), followed by E and D. The unbleached pulp is treated with Cl₂, with or without ClO₂ reinforcement in the first C tower. The pulp enters at the bottom of the first C tower, flowing upwardly through the tower and discharging at the top of the tower into a washing section wherein it is washed with water. The washed pulp is discharged from the washer via line 14, sodium hydroxide being added thereto. Line 14 discharges the thus alkalinized pulp into a steam mixer 15 by which it is brought to a temperature in the range of 40-70° C. The thus heated pulp is pumped at 15 into the top of the E tower 16, where it is subjected to alkaline extraction followed by water washing as indicated at 18.

The washed pulp is then pumped, at 20, into the bottom of the first D tower 22 and flows upwardly through that tower in which it is treated with ClO₂. Following the ClO₂ treatment, the pulp is again washed with water at 24 and pumped into the top of the second E tower 25 with addition of sodium hydroxide. Discharged from the bottom of tower 25 the pulp is again washed in water at 26 and introduced into the bottom of the second D tower 28 for a second treatment with ClO₂; the thus bleached pulp discharged from the top of tower 28 being water washed at 29.

The conventional 5 stage system (C_0E_0D) of Figure 1 is often replaced by a short three stage sequence (C_0E_0D); see Enz, et al., TAPPI Proceedings, 1983 Pulping Conference, pages 309-313; Boussard, et al., op. cit., pages 315-317). The three stage sequence without loss in pulp quality was made possible by introduction of molecular oxygen into the pulp entering the thus modified alkali extraction stage ("oxygen alkali extraction") designated by the symbol E_0 , illustrated in Figure 2, like parts bearing the same reference characters as in Figure 1 wherein applicable. As shown in Figure 2, an O_2 /pulp mixer or O_2 diffuser 30 is provided in the line feeding the E_0 tower.

In practice of the present invention employing the short sequence of Figure 2, the operating conditions of C and E_0 stage are modified by:

- (a) reduction in dosage of chlorine employed to KF 0.11 to 0.20,
- (b) increasing the temperature of the alkaline under chlorinated pulp by adding more steam to the pulp at the steam mixer in line 14, to raise exit pulp temperature to 85-100° C, and
- (c) adding at least about 0.3% hydrogen peroxide to the pulp just before or after introduction of the molecular oxygen thereto, which is also increased to about 0.8-1.2% by weight on dry pulp. The peroxide may be added, for example, to the washed pulp in line 14 together with or preceding the alkali addition, or subsequently thereto at the steam mixer, but preferably at pump 15, or alternatively at a point in line just prior or after the pulp/ O_2 mixer or diffuser 30.

While in Figure 2, the practice of the invention is described as applied to the C_0E_0D sequence, it will be understood that the invention is not limited thereto but can be employed to advantage in the 5 stage sequence or in any bleach sequence having an oxygen alkali extraction stage following the chlorination stage with attending reduction of the otherwise required amount of Cl_2 and/or ClO_2 needed to be employed. The advantages of the invention are easily obtained without loss of desirable pulp brightness, while achieving the benefits of oxygen bleaching, chlorine dioxide substitution, and hot alkali extraction, without the attendant high capital and added chemical costs, and without requiring any major change in the existing process configuration. Not only are environmental benefits achieved such as reduced effluent TOC/AOX due to the reduced amount of applied Cl_2 , net chemical savings are also realized by the invention since the required amounts of both chlorine and also the more expensive chlorine dioxide, are significantly reduced.

A primary objective of the present invention is to enable reduction in the required amount of chlorinating agent needed to be employed in delignification and bleaching of lignocellulosic pulp to obtain the desired product without adverse effect on pulp brightness or viscosity, while avoiding the otherwise negative impact on environment of chlorine-based bleach plant effluents.

There is generally a linear relationship between increasing chlorine application (dosage) and the pulp lignin content, which may be expressed in terms of Kappa number. The higher the Kappa number of the pulp the greater the chlorine dosage needed to delignify the pulp. Typical for kraft softwood, for example, industry employs 6 to 8% chlorine by weight on dry pulp. The amount of molecular chlorine required for effective delignification of the pulp of a given Kappa number is expressed by the Kappa factor (KF), thus

$$KF = \frac{\% Cl_2}{\text{Kappa No.}}$$

Use of less chlorine results in unacceptable pulp of low brightness.

Since ClO_2 is frequently added to the pulp at the C stage, the quantity of actual molecular chlorine can be reduced by substitution of the active chlorine equivalent with ClO_2 , so

$$KF = \frac{\% Cl_2 + 2.63 (\% ClO_2)}{\text{Kappa number}}$$

In the delignification of unbleached lignocellulosic pulp a Kappa factor in the range of 0.21 to 0.23 is typically advocated and employed in mill practice, based on actual plant experience to provide a balance between sufficient delignification and minimizing subsequent/downstream chemical requirement to achieve target brightness.

To demonstrate the advantages afforded by the present invention, results from several bleaching sequences were compared. The basic C_0E_0D three-stage sequence was selected for demonstration purposes in all of the reported runs since it is a common commercial sequence and it is an accepted

laboratory standard in the industry. The operating conditions employed in the demonstration are represented by:

$C_D E_O D$ which is representative of a common three-stage sequence with chlorine dioxide substituted for some chlorine in the chlorination stage as is common practice in the art and employing a conventional oxygen alkali extraction stage (3-5 minutes oxygen contact time, 20-25 psig, and 60-70 °C).

This is the reference sequence in which it is demonstrated that total chlorine charge (C+D) in the chlorination stage can be reduced by practice of the invention. In this reference experiment, a total chlorine charge of 7.5% is used at 15% dioxide substitution (6.38% Cl_2 + 1.13% D as active chlorine).

$$KF = \frac{6.38 + 1.13}{32.7} = 0.23$$

$C_D E_O D$ Also the reference three-stage sequence in which the chlorine in the chlorination stage was reduced without obtaining benefit of the present invention.

$C_D E_O^* D$ Also the reference three-stage sequence, except the reaction parameters of the E_O stage are modified/enhanced in concert with a reduction in either or both chlorine and chlorine dioxide in the chlorination stage.

In the experimental runs set out below, commercial, unbleached southern pine softwood kraft pulp (brownstock) was used. The initial Kappa number was 32.7 and exhibited a 0.5% CED viscosity of 20.6 centipoise (cp). The operating conditions employed are summarized below.

A. Standard Chlorination (C_D) Stage:

Crumbled pulp was placed in a polyester bag and an amount of chlorine water and chlorine dioxide added to make the charge 6.38% and 1.13%, respectively, as active chlorine. Dilution water was then added to bring the pulp to a consistency of 3.5%. The bag was heat sealed and the chlorination allowed to proceed at ambient temperature for 45 minutes. The pulp was filtered (effluent pH 1.7 to 1.8) and washed with water.

B. Conventional and Reinforced Oxygen Alkali Extraction (E_O) Stage:

The oxygen reaction vessel was a direct steam-heated pressure vessel containing a removable rack upon which seven circular stainless steel mesh trays are arranged, one above the other. The trays allow thin layers of pulp to be dispersed within the vessel so as to provide intimate contact with oxygen in order to simulate good O_2 /pulp contact available in the bleach plant.

While the reactor was preheating, sufficient water, chlorinated pulp, and alkali (NaOH) were mixed to bring the consistency to 12% and alkali charge to 3.64%. When peroxide, magnesium sulfate, or hypochlorite were to be added, these chemicals were also mixed with the pulp at this time.

After the pulp samples were placed on the vessel's removable trays, the assembly was placed in the preheated reactor which was then bolted closed and the temperature raised immediately (<2 minutes) to 70 °C. Oxygen was then added to the reactor at 25 psig. After 5 minutes' exposure to oxygen, the oxygen was vented and the extraction was allowed to proceed an additional 55 minutes (total time never exceeded 60 minutes) without oxygen to complete the extraction stage. The separate pulp samples were then removed, washed with water, and prepared for the dioxide bleaching stage.

C. Chlorine Dioxide Bleach (D) Stages:

Each individual pulp sample removed from the trays of the extraction reactor was subjected separately to different levels of dioxide charge in order to determine the bleaching performance profile, i.e., brightness vs. dioxide charge.

The extracted pulp sample was placed in a polyester bag and a calculated amount of aqueous chlorine dioxide added (usually 0.5 to 2.0% on pulp) followed by sufficient water to bring pulp consistency to 10%. The bag was sealed and rapidly brought to 70 °C and maintained at this temperature for 3 hours. At this time, typically an aliquot of bleach liquor was also removed and analyzed for residual dioxide. The dioxide bleached pulp was then treated with sulfur dioxide to bring the pH to 3 prior to forming handsheets for brightness measurements.

Results are graphically represented as brightness versus dioxide charge which is a measure of the ability of this sequence to achieve target brightness.

Kappa number (T236), viscosity (T230), handsheets (T218), and brightness (T217) determinations were made in accordance with the respective TAPPI Standard Test Procedure identified by the numbers in parentheses. Chemical charges are on a weight percent basis; pulp weight is reported on an air dry basis.

Example 1: Control Experiment and Reference/Standard $C_D E_O D$ Sequence with Conventional E_O Stage

The purpose of this control example is to determine the required amount of dioxide to achieve a given brightness level for conventionally chlorinated pulp at $KF = 0.23$, and to show what maximum brightness level could be achieved at conventional $C_D E_O D$ bleach conditions for this brownstock pulp.

Following the general procedures outlined above, commercial brownstock of Kappa number 32.7 and a viscosity of 20.6 cp was subjected to chlorination (6.38% Cl_2 + 1.13% ClO_2 as active chlorine, $KF = 0.23$) and conventional oxygen alkali extraction (3.64% $NaOH$, 70°C, 5 minutes O_2 at 25 psig, balance of 60 total minutes with no oxygen) stages. The washed pulp from the $C_D E_O$ stage was divided into 4 portions and subjected to different dosages of chlorine dioxide at a pH of 3.8-4.3 to complete the $C_D E_O D$.

TABLE 1(a)

% D	Brightness	Viscosity
0.5	72.5	20.7
0.8	79.8	21.0
1.0	83.9	20.5
1.3	85.6	20.1

Example 2: Demonstration of Loss of Final Brightness that would be Observed with and Reduction in Chlorine Charge without any Modification of E_O Stage ($C_D E_O D$)

The experiment described in example 1 was repeated except that the molecular chlorine charge was reduced by 20%; the chlorine dioxide charge was maintained at the amount used in example 1 so the effective ClO_2 substitution level was of course higher in this experiment. The Kappa Factor (KF) was 0.18, or 22% lower than the conventional chlorination of Example 1.

TABLE 1(b)

% D	Brightness	Viscosity
0.5	57.4	19.0
0.8	69.0	20.3
1.0	73.4	20.3
1.3	78.6	19.6

These results are graphically presented in Figure 3 along with those of the control experiment (example 1). It is clearly seen that commercially unacceptable pulp (severe brightness loss) results from the environmentally desirable act of reducing the chlorine consumption in the chlorination stage, even if one increases the level of dioxide substitution in the chlorination stage.

Example 3-6: Demonstration That Pulp Brightness Cannot be Maintained at Reduced (20%) Cl_2 Charge Even at Increased Dioxide Substitution and Several Common Enhancements to the Conventional E_O Stage ($C_D E_O^+ D$)

The purpose of this series of experiments, the results of which are summarized in Figure 4 along with the control tests of examples 1 and 2 for comparison, is to demonstrate that at a reduced chlorine dosage

of only 20%, one cannot maintain target/acceptable pulp brightness even at higher chlorine dioxide substitution levels, simply by modifying conventional E₀ stage process conditions to longer oxygen contact times (5 minutes to 20 minutes) or, even at this extended contact time, by increased E₀ stage temperature (70-100 °C), or addition of hypochlorite or hydrogen peroxide to the E₀ stage.

Examples 3-6 were performed as described in example 2 where the chlorine charge alone was reduced by 20% with the chlorine dioxide level maintained at the same (example 1) chlorination stage level so, in effect, to increase the dioxide substitution level to greater than the initial 15%. Otherwise, only the E₀ stage parameters were changed as described below, with the results compared in Table 2.

TABLE 2

	Example	Brightness at Respective Dioxide Dosage			
		0.5%	0.8%	1.0%	1.3%
Ex. 3 graph 4c	Extend O ₂ contact time of E ₀ stage from conventional 5 to 20 minutes.	62.5	73.2	76.2	81.7
Ex. 4 graph 4d	E ₀ stage temperature increased from conventional 70 °C:				
	(1) to 100 °C, O ₂ contact time - 20 minutes.	68.6	78.2	81.5	84.2
	(2) to 110 °C, O ₂ contact time - 20 minutes.	63.6	75.0	79.4	82.0
NOTE: Higher temperature (above 100 °C) gives poorer results.					
Ex. 5 graph 4e	0.7% sodium hypochlorite added to E ₀ stage; O ₂ contact time - 20 minutes.	59.5	70.0	73.4	78.4
Ex. 6 graph 4f	0.7% hydrogen peroxide added to E ₀ stage; O ₂ contact time - 20 minutes.	69.4	77.2	81.5	83.8

As seen in Figure 4, bar graphs 4a and 4b show the brightness of pulp after receiving treatment under conditions of Examples 1 and 2, respectively, (83.9 at full chlorine dosage and 73.4 at 20% reduction in chlorine dosage). Bar graph 4c shows that the loss in brightness at lowered chlorine dosage is not compensated by extension of the time of exposure to added oxygen (Example 3). Bar graph 4d shows that some further increase in brightness is had by raising the temperature of the E₀ stage to 100 °C or 110 °C (Example 4) while maintaining the oxygen exposure at 20 minutes. Example 5 (bar graph 4e) carried out at the conventional E₀ temperature (70 °C) at extended time of O₂ exposure (20 minutes) but with addition of hypochlorite to the E₀ stage does not achieve acceptable brightness. Nor is desired brightness achieved by using hydrogen peroxide additive in the E₀ stage (Example 6). The results of Examples 3 to 6 are summarized in Table 2.

Example 7-8: Demonstration that Pulp Brightness can be Maintained with 20% Less Chlorine by Both Adding Peroxide and Increasing Alkaline Pulp Temperature Prior to Addition of Oxygen in the E₀ Stage

The experiment described in example 2, which reduced chlorine by 20% while maintaining the same dioxide level in the chlorination stage, was repeated except 0.7% hydrogen peroxide was added to the alkaline pulp which was then heated to 100 °C prior to contacting with pressurized oxygen at 25 psig for 5 minutes (example 7) and 20 minutes (example 8).

The results are tabulated below in Table 3 and summarized in Figure 5 along with the control tests of examples 1 and 2 for comparison. The results clearly show this unique and specific condition allows a reduction in chlorine charge without resorting to long oxygen contact times unavailable to existing conventional E₀ systems. Furthermore, if longer O₂ contact times were made available, only incrementally

higher brightness levels could be achieved at the reduced chlorine charge.

Table 3

	<u>% D</u>	<u>Pulp Brightness</u>	
		<u>Example 7</u> <u>(5 mins O₂ Contact)</u>	<u>Example 8</u> <u>(20 mins O₂ Contact)</u>
10	0.5	70.1	80.1
	0.8	80.5	86.1
15	1.0	84.9	86.4
	1.3	86.2	87.4

20 Example 9-11: Demonstration that the Pulp Properties of Brightness, Viscosity, Cleanliness, and the Quality of the E₀ Stage Effluent can be Maintained with a 30% Reduction in Chlorine and 100% Reduction/Elimination of Chlorine Dioxide in the Chlorination Stage

25 $(C_D E_0 D \text{ vs. } C_{E_0 D}^*)$

For purposes of this demonstration, a new control (base case, example 9) was simultaneously
30 completed along with two experiments (examples 10 and 11) that demonstrate the technology at 0.4 and 0.5% hydrogen peroxide charges (prior examples used 0.7% peroxide). The results are tabulated below and summarized in Table 7 showing that within experimental error, final pulp quality (brightness, viscosity, and shives) and effluent quality from the E₀ stage are maintained at 30% reduction of chlorine and with elimination of the ClO₂ in the chlorination stage. The data also suggests 0.3% peroxide will be minimum
35 required dosage.

Example 9 - New Control

40 The bleach sequence experiment described in example 1 was repeated except at a molecular chlorine charge of only 6.19% and a dioxide charge of only 0.414% (KF = .20). Results are reported in Table 4.

Table 4

	<u>E₀</u> <u>Stage</u>	<u>D-Stage</u>					
		<u>0.5%</u>	<u>0.8%</u>	<u>1.0%</u>	<u>1.3%</u>	<u>1.6%</u>	<u>2.0%</u>
45	Viscosity	20.5					
	Color	35,250					
50	BOD-5	158					
	COD	1,424					
	Brightness	71.7	82.4	85.4	87.3	88.2	88.5
	Viscosity	20.2	---	19.0	19.6	19.4	18.2
55	Shives	---	---	---	425	400	325

Example 10

Experiment/example 9 was repeated except with 30% less Cl_2 (4.33% Cl_2) and no chlorine dioxide in the chlorination stage. The Kappa Factor was only 0.13, or 35% less than the conventional chlorination in Example 9. The temperature of the E_0 stage was increased to only 90 °C and only 0.4% peroxide added prior to the oxygen. Oxygen contact time and pressure were maintained at 5 minutes and 25 psig. Results are reported in Table 5.

Table 5

	<u>E₀</u> <u>Stage</u>	<u>D-Stage</u>					
		<u>0.5%</u>	<u>0.8%</u>	<u>1.0%</u>	<u>1.3%</u>	<u>1.6%</u>	<u>2.0%</u>
Viscosity	20.9						
Brightness		60.8	73.1	78.2	83.1	85.1	85.6
Viscosity		18.9	19.3	19.0	19.0	17.6	16.8
Shives		---	---	---	---	375	575

Example 11

Experiment/example 10 was repeated except with 30% less Cl_2 and no chlorine dioxide in the chlorination stage (KF = 0.13). The temperature of the E_0 stage was increased to only 90 °C and only 0.5% peroxide added prior to the oxygen. Oxygen contact time and pressure were maintained at 5 minutes and 25 psig. Results are reported in Table 6.

Table 6

	<u>E₀</u> <u>Stage</u>	<u>D-Stage</u>					
		<u>0.5%</u>	<u>0.8%</u>	<u>1.0%</u>	<u>1.3%</u>	<u>1.6%</u>	<u>2.0%</u>
Viscosity	21.3						
Color	36,375						
BOD-5	161						
COD	1,478						
Brightness		66.3	79.1	81.9	84.6	86.0	86.9
Viscosity		18.3	18.0	18.6	17.7	16.1	16.4
Shives		---	---	---	300	225	225

The results of Examples 9-10 are compared in Table 7. Final brightness is shown after 2% ClO_2 treatment in the D stage as well as shives count.

Effect of both increased temperature and peroxide addition before oxygen on the final pulp properties and E_0 stage effluent in $\text{C}_0\text{E}_0\text{D}$ bleaching at reduced Cl_2 and ClO_2 in chlorination stage (35% lower Kappa Factor), is seen in Table 7 below:

Table 7

	(Ex. 9)	(Ex. 10)	(Ex. 11)
	<u>C_DE_OD</u>	<u>CE_OD</u>	
	Conventional E _O at 70 ° C, 5 min O ₂ No Peroxide	30% Cl ₂ Reduction Elimination of ClO ₂	
		E _O at 90 ° C, 5 min O ₂	
<u>E_O Stage</u>		0.4% Peroxide	0.5% Peroxide
Pulp Viscosity	20.5	20.9	21.3
Effluent, Color	35,250	--	36,375
BOD-5	158	--	161
COD	1,424	--	1,478
<u>D-Stage at 2% ClO₂</u>			
Pulp Brightness	88.5	85.6	86.9
Pulp Viscosity	18.2	16.8	16.4
Pulp Shives	325	375-575	225

Example 12: Demonstration that Observed Results are not a Tradeoff on the Benefits to Conventional E_O - (C_DE_OD vs. C_DE_O*D)

This experiment follows Nonni, U.S. 4,568,420 of reinforcing the conventional E_O stage with H₂O₂, except that the temperature of the E_O stage is increased to 90 ° C.

The experimental bleach sequence described in example 9 (full charge of Cl₂ + ClO₂ in chlorination stage) was repeated except the temperature of the E_O stage was increased to 90 ° and 0.5% peroxide added. The results are tabulated below and summarized in Figure 6 along with the control, example 9, accomplished at conventional E_O conditions. The similarity of this brightness vs. dioxide dosage and bleaching curve show, as expected, that this proposed new chlorine reduction technology is different and not simply a variation on reinforced oxygen alkali extraction, as seen in Table 8.

Table 8

<u>% D</u>	<u>Control Ex. 9</u>	<u>This Example 12</u>	
		<u>Brightness</u>	<u>Viscosity</u>
0.8	82.4	85.2	20.4
1.0	85.4	86.8	20.1
1.3	87.3	87.8	19.3
1.6	88.2	88.2	18.1
2.0	88.5	88.6	16.9

No advantage is gained in brightness at the elevated temperature as expected from the Nonni examples and B. Van Lierop, et al. Proceedings 1985 International Pulp Bleaching Conference, page 83, which states there is no advantage to operating an E_O system above 50 ° C.

As demonstrated in our invention, a surprising temperature effect is observed only when chlorinating agent is reduced.

The beneficial advantages of the present invention are realized when the herein advocated process conditions are utilized in the treatment of unbleached pulp (CE₀... sequence) as well as in the delignification/bleaching of a pulp which has been oxygen prebleached (OCE₀...). Moreover, the addition of a magnesium compound (MgSO₄) or other stabilizer deemed essential in prior pulp treatment to avoid pulp degradation, may be omitted when practicing the present invention.

In general, the desired reduced chlorination bleach process of the present invention can be achieved by reducing the needed chlorinating agent (molecular chlorine with or without chlorine dioxide) dosage to that required to maintain a Kappa factor in the range of 0.11 to 0.20, employing selected operating conditions not conventional in the oxygen alkali extraction stage (E₀) following the initial under chlorination at reduced

KF, said conditions including:

- (1) increasing oxygen to the total amount of 0.8 to 1.2 percent by weight of pulp (dry basis) and at a pressure of 20 to 70 psig; higher oxygen dosage (beyond about 1.5%) can be used without added advantage. Oxygen contact time should be 3 to 5 minutes at 20-25 psig.
- (2) use of temperatures above that commonly employed in the art, preferably above 85° C and up to about 100° C. Temperature above 100° C obtain no added advantage, and can have adverse effect on pulp quality.
- (3) addition of at least 0.3% and no more than about 1% hydrogen peroxide by weight of pulp (dry basis).

All of the above conditions (1) higher oxygen dosage, (2) higher temperature, (3) minimum peroxide dosage indicated, must be observed to maintain desired brightness at the reduced chlorination dosage (reduced Kappa Factor). No benefit is observed in bleaching without reduced chlorine dosage as shown in Example 12.

Claims

1. In the delignification and bleaching of lignocellulosic pulp wherein the unbleached pulp or oxygen pretreated pulp is treated in successive stages with various delignification and bleaching chemicals including in sequence an initial chlorination stage with a chlorinating agent comprised of chlorine dioxide or of molecular chlorine with or without added chlorine dioxide, followed in turn by alkali extraction in the presence of added molecular oxygen, the improvement which comprises: utilizing in said initial chlorination stage an amount of chlorinating agent corresponding to a Kappa factor equal to or less than 0.2, performing said alkali extraction at a temperature of at least 85° C with the molecular oxygen being at a dosage of at least 0.8% by weight of air dried pulp and with the addition therein of at least 0.3% hydrogen peroxide by weight of pulp on a dried pulp basis.
2. The improvement as defined in Claim 1 wherein the initial chlorination stage is performed with an amount of chlorinating agent corresponding to a Kappa factor in the range of 0.11 to 0.18.
3. The improvement as defined in Claim 1 wherein said alkali extraction is carried out at a temperature in the range of 85° to 100° C.
4. The improvement as defined in Claim 3 wherein the hydrogen peroxide addition is no more than 1% by weight of the pulp.
5. The improvement as defined in Claim 4 wherein the hydrogen peroxide is added to the pulp prior to the molecular oxygen.
6. The improvement as defined in Claim 5 wherein following the recited alkali extraction stage the pulp is subjected to one or more additional bleaching stages.
7. The improvement as defined in Claim 6 wherein at least one of said bleaching stages is performed using chlorine dioxide.
8. The improvement as defined in Claim 7 wherein during said alkali extraction stage molecular oxygen is introduced for up to five minutes at a pressure of about 25 psig.
9. The improvement as defined in Claim 8 wherein said alkali extraction is effected during a total period of 60 minutes.
10. The improvement as defined in Claim 1 wherein the initial chlorination stage is performed with molecular chlorine without addition of chlorine dioxide, said molecular chlorine being applied in an amount corresponding to a Kappa factor of 0.13, and wherein 0.4 to 0.5% hydrogen peroxide by dry weight of pulp is used in the alkali extraction stage.
11. The improvement as defined in Claim 1 wherein said initial chlorination is carried out under conditions corresponding to a Kappa factor of 0.20 and said alkali extraction is carried out at 90° C with the addition of 0.5% peroxide by weight of dry pulp, followed by at least one bleaching step using chlorine dioxide.

12. The improvement as defined in Claim 11 wherein in said alkali extraction the molecular oxygen is introduced for about five minutes at a pressure of about 25 psig, after which the extraction is continued in the absence of additional oxygen for up to about a total period of about sixty minutes.

13. The improvement as defined in Claim 1 wherein said alkali extraction is performed in the absence of
5 magnesium compound or other added stabilizer for retarding pulp degradation.

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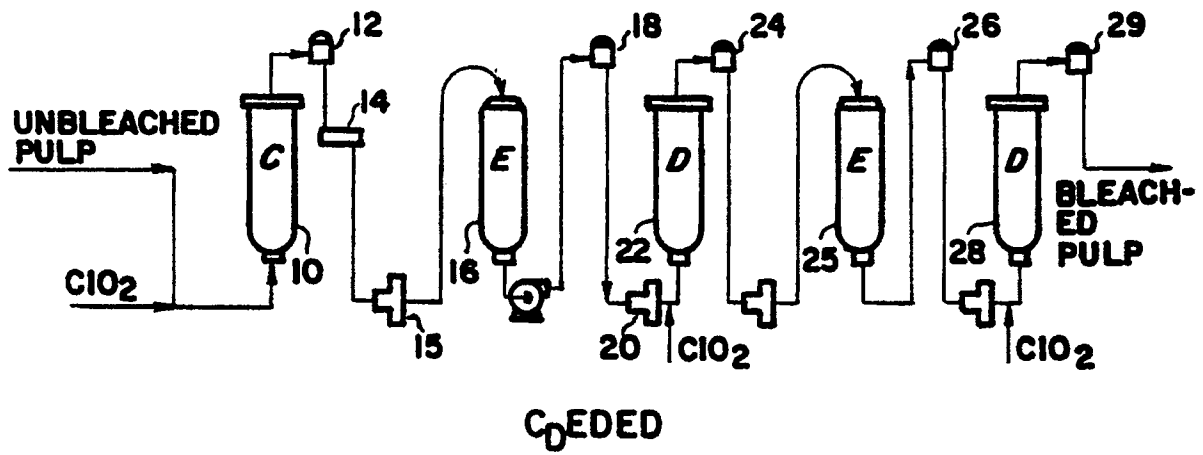


FIG. 1

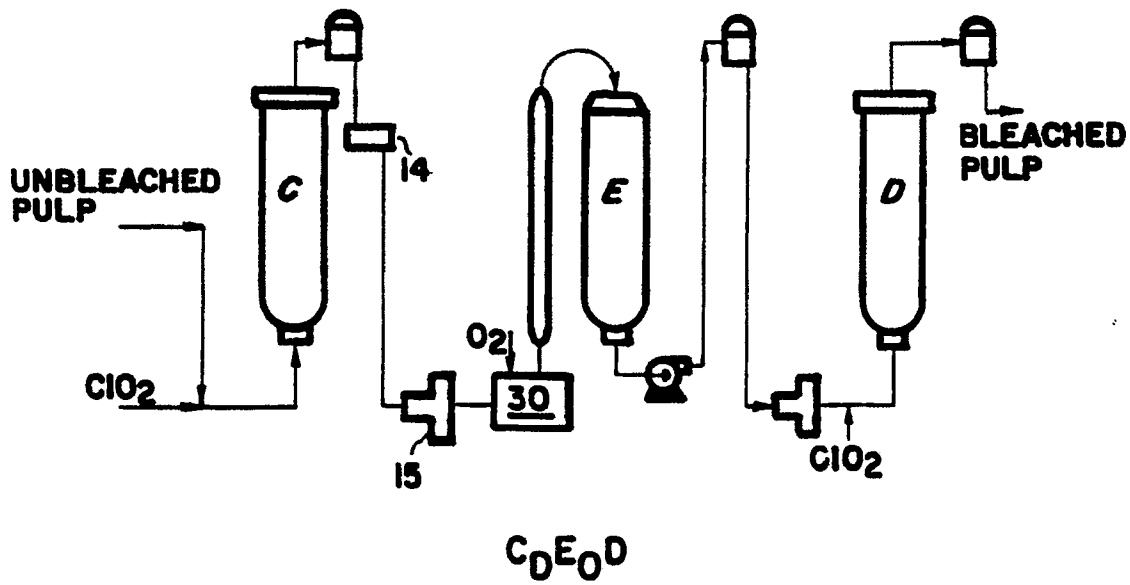


FIG. 2

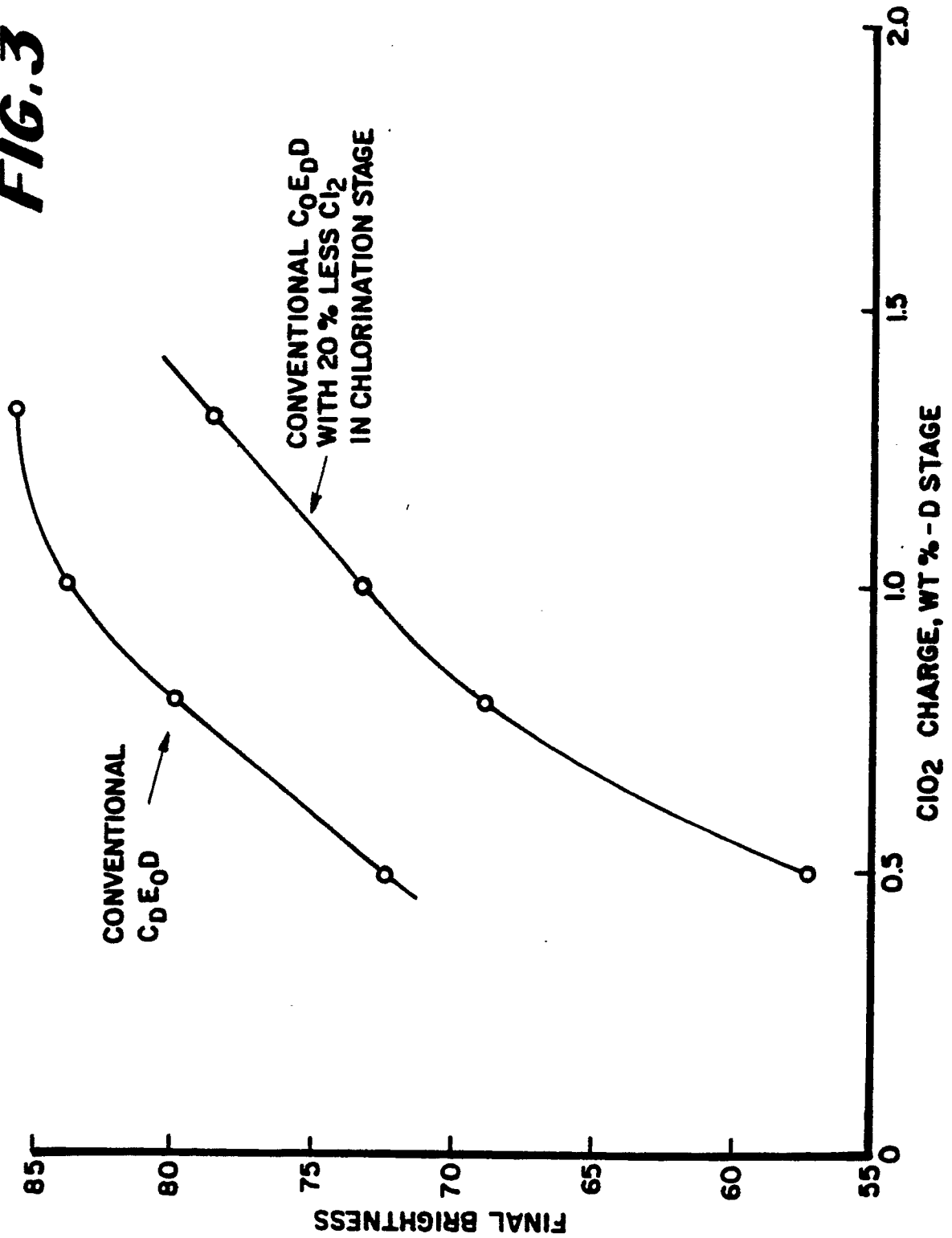
FIG. 3

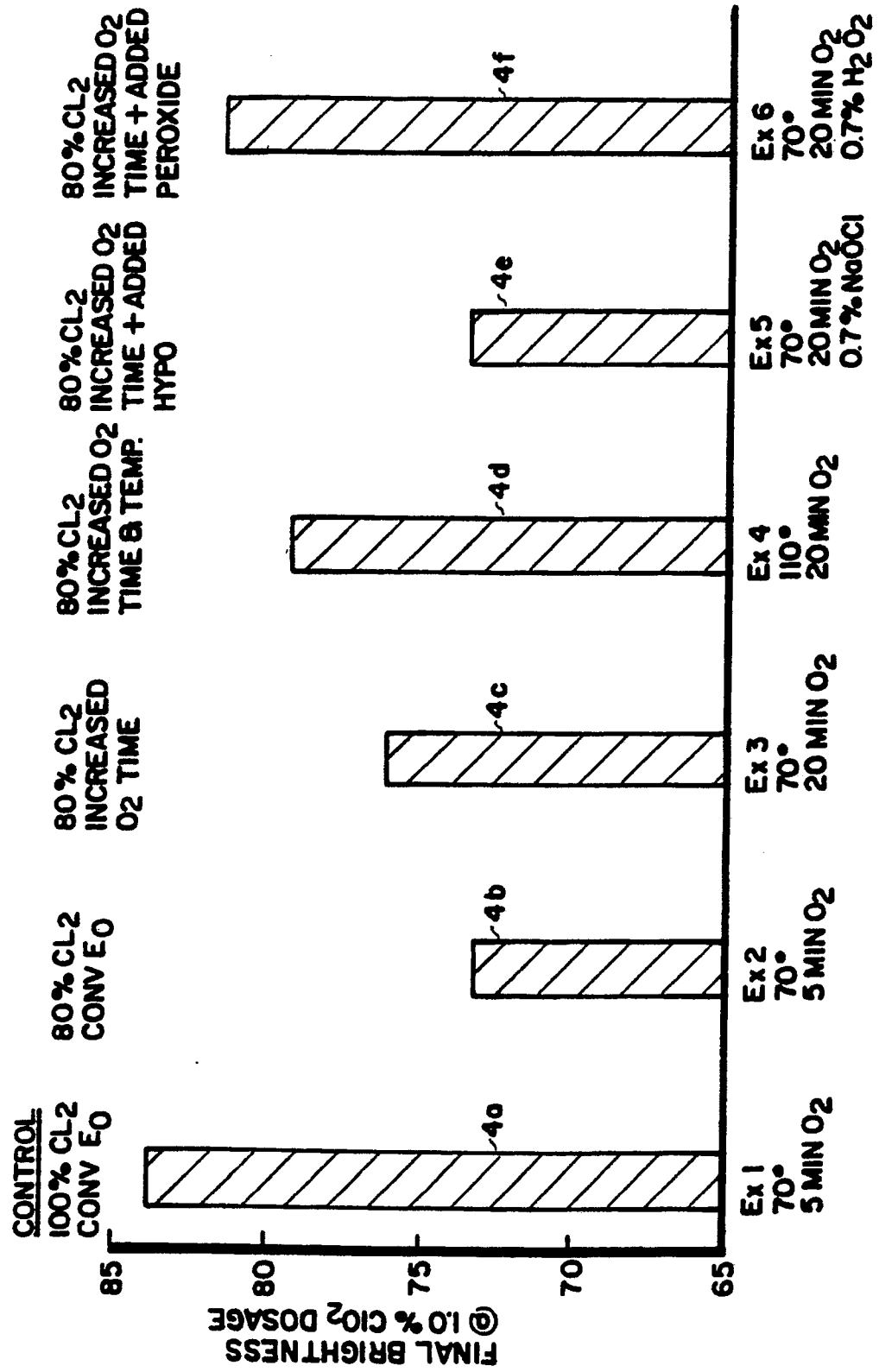
FIG. 4

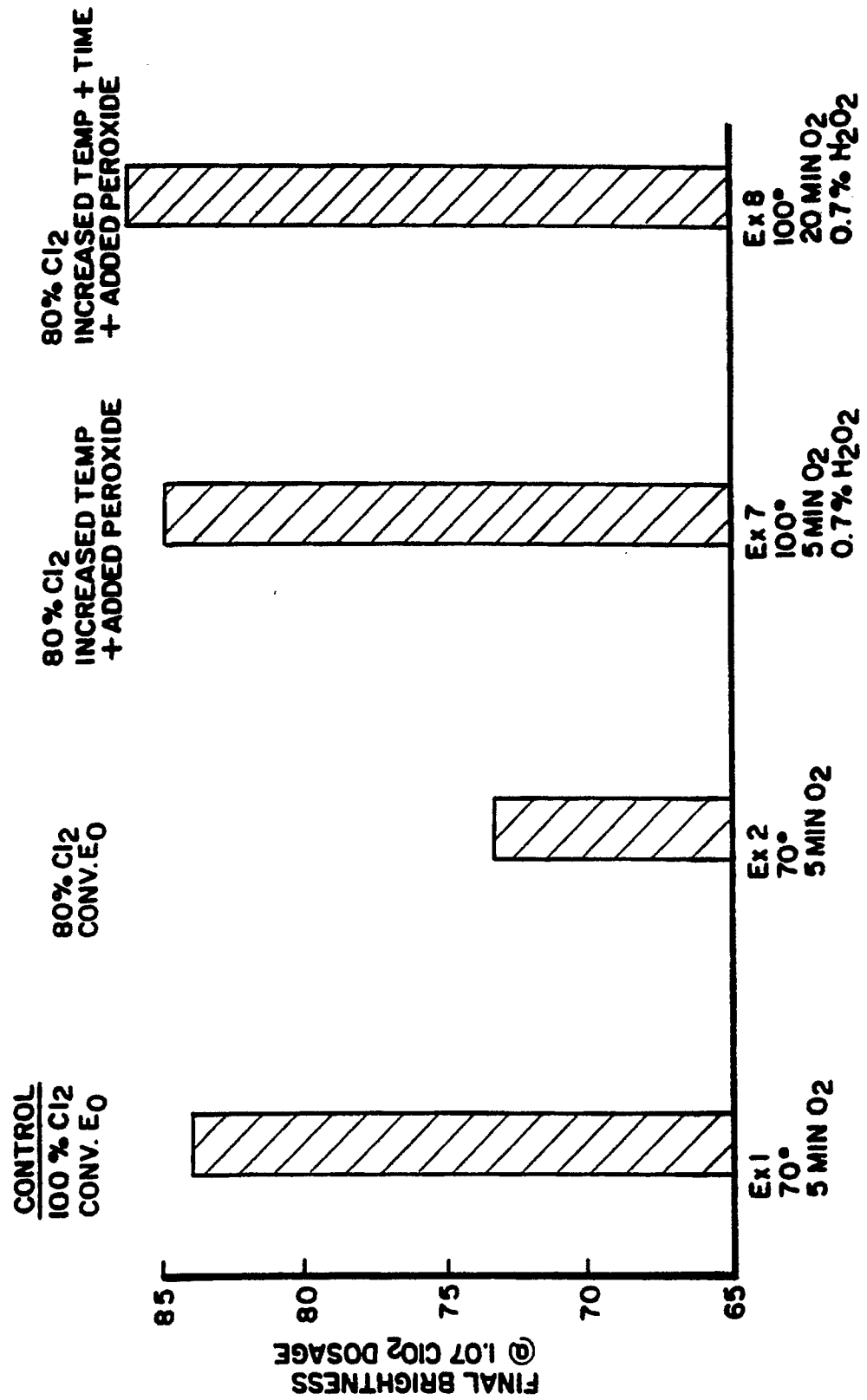
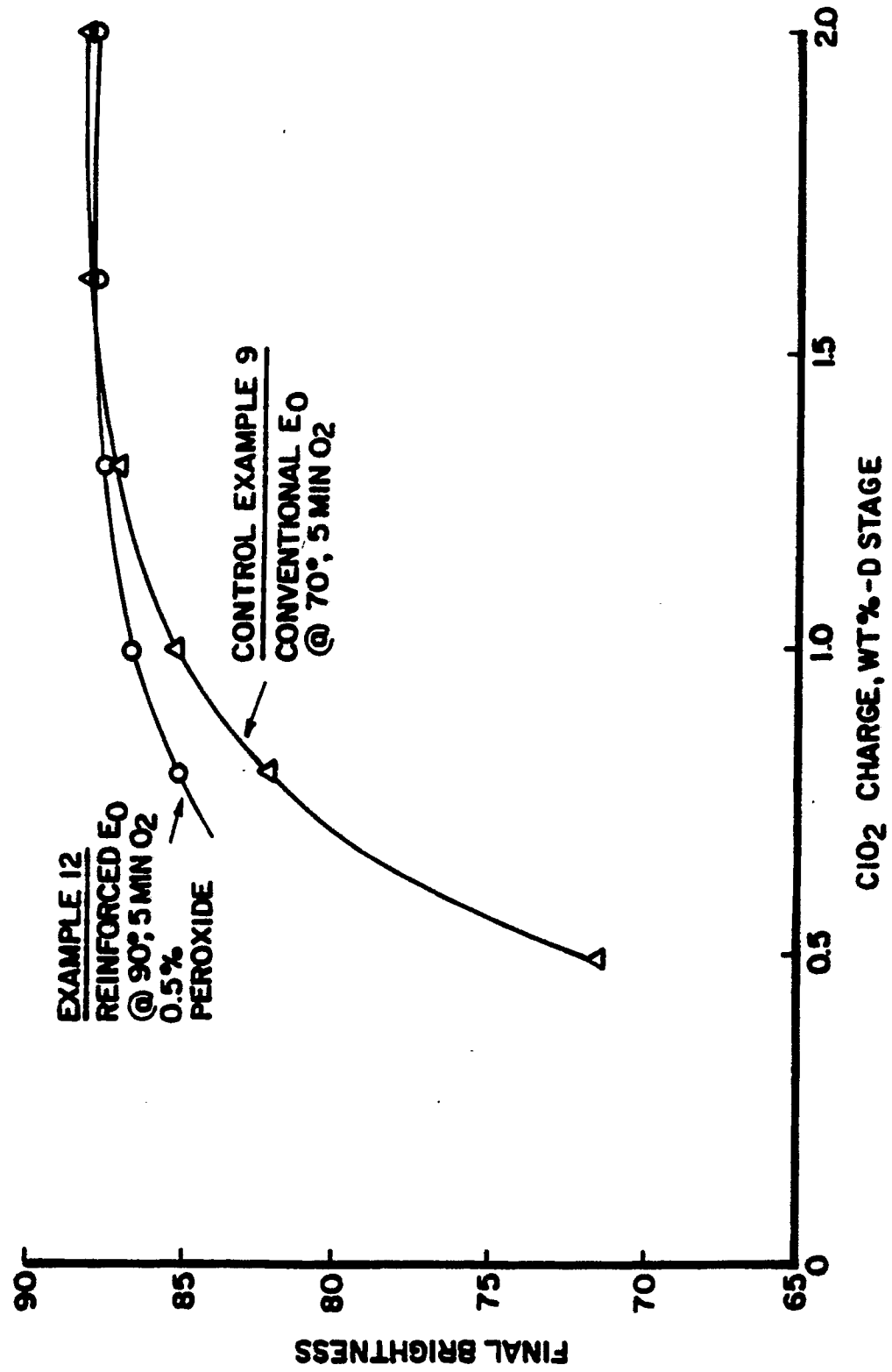
FIG. 5

FIG. 6

EP 90 11 6168

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,A	EP-A-0 206 560 (PULP AND PAPER RESEARCH INSTITUTE OF CANADA) * column 3, line 35 - column 5, line 37 * examples 7,8; claims *	1-4,6,7,9, 8,10,11, 13	D 21 C 9/10 D 21 C 9/147 D 21 C 9/16
D,A	US-A-4 568 420 (INTERNATIONAL PAPER COMPANY) * column 3, line 47 - column 4, line 41; claims 1, 6-19 *	1,4-7,13	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 21 C
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		06 March 91	BERNARDO NORIEGA F.
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention		E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document	