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(54) HIGH EFFICIENCY CHLORINE DIOXIDE PULP BLEACHING PROCESS

HOCHLEISTENDES VERFAHREN ZUM BLEICHEN VON ZELLSTOFF MIT CHLORDIOXYD

PROCEDE DE BLANCHIMENT DE CELLULOSE HAUTEMENT EFFICACE A L'AIDE DE DIOXYDE DE CHLORE

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(56) References cited:
DE-A- 3 239 811 **US-A- 3 433 702**
US-A- 4 274 912

- **Pulp & Paper Canada (REEVE et al) December 1981 "The Effluent-Free Bleached Kraft Pulp Mill Part XII", See Figure 2.**
- **Journal Pulp & Paper Science (MACAS et al) 03 May 1987 "The Effect of Chlorine in the D. Stage" Volume 13, No. 3, See Page J107.**
- **TAPPI JOURNAL (ENZ et al) June 1984 "Oxidative Extraction: An Opportunity for Splitting the Bleach Plant". See Page 57.**
- **A. Wong, Effect of Tetrahydroanthraquinone (THAQ) on the Neutral Sulphite Pulping of Seed Flax Fibres, Journal of Pulp and Paper Science: Vol. 13 No. 1, Jan 1987. A. Teder and Lisa Tormund, Carbohydrate degradation in chlorine dioxide bleaching, Tappi, Vol. 61, No 12, Dec 1978**

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The file contains technical information submitted after the application was filed and not included in this specification

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Description

The present invention relates to the bleaching of pulp and more particularly to an improved process for bleaching wood pulp with chlorine dioxide in a manner whereby the wood pulp is subjected to a 2-step high pH/low pH bleaching stage which results in a substantial decrease in the usage of chlorine dioxide required to brighten wood pulp.

As is well known in the wood pulp bleaching art, the main objectives of wood pulp bleaching are to increase the brightness of the pulp and to make it suitable for the manufacture of printing and tissue grade papers by removal or modification of some of the constituents of the unbleached pulp, including the lignin and its degradation products, resins, metal ions, non-cellulosic carbohydrate components, and various other types of flecks. The bleaching of chemical wood pulp is normally carried out in multiple processing stages utilizing elemental chlorine, caustic soda, hypochlorites, oxygen, hydrogen peroxide, and chlorine dioxide. The number of stages required in a particular bleaching process is dependent upon the nature of the unbleached pulp as well as the end use to which the pulp will be put.

DE-A-3239811 discloses a process for bleaching cellulose-containing materials in a multi-stage sequence. The cellulose-containing materials are treated with chlorine (Cl_2) under careful pH control, followed by chlorine dioxide.

An article in the Journal of Pulp and Paper Science, volume 13, No. 1, January 1987, Annergren, Häggkvist and Lindblad, discloses chlorine dioxide bleaching carried out for extended reaction times in order to achieve a low residual chlorine dioxide level.

An article in Tappi Journal, volume 61, No. 12, December 1979, Teder and Tormund, discloses a chlorine dioxide stage having distinct steps, the first employing a pH of up to 6, for 5 or 6 minutes as a pre-treatment, prior to bleaching at a pH of 4 to 5, for 35, 80, 85 or 115 minutes. The purpose is to inhibit carbohydrate degradation.

U.S.-A-3433702 discloses a process employing a chlorine dioxide stage followed by a chlorination stage, instead of a chlorination stage followed by a chlorine dioxide stage, as is conventional.

Notwithstanding the prior disclosures referred to in the previous four paragraphs, a sulphate or kraft pulp is today most typically bleached in a five stage sequence which is designated as (CD)(EO)DED. In the (CD)(EO)DED designation, D denotes chlorine dioxide, C denotes elemental chlorine, E denotes caustic extraction, and O denotes oxygen gas. The multi-stage process in essence comprises a chlorination step (CD), a first oxidative extraction stage (EO), a first bleaching stage (D_1), a second caustic extraction stage (E_2), and a second and final bleaching stage (D_2).

In the conventional (CD) (EO)DED multi-stage bleaching process, each of the two chlorine dioxide bleaching stages is carried out in an one-step process at an end pH of about 3.8 for three hours at 70°C. It is commonly known that pH has an important bearing on brightness and strength properties as well as the chemical species present in the wood pulp mixture, and this particular pH has heretofore been considered optimal for each of the two chlorine dioxide bleaching stages in the (CD)(EO)DED sequence. It should also be appreciated that although the (CD) (EO)DED sequence has been specifically addressed, the one-step chlorine dioxide bleaching stage can be used in any D stage for most other three, four, five or six-stage bleaching processes known to those familiar with the art of wood pulp bleaching.

A shortcoming of the one-step chlorine dioxide bleaching stage presently used in the pulp and paper industry is that approximately 30% of the chlorine dioxide is lost to the formation of the unreactive species chlorite and chlorate, and this is very undesirable in view of the relatively high cost of chlorine dioxide. The present invention solves this well-known deficiency in state of the art chlorine dioxide bleaching by significantly reducing the chlorine dioxide loss during the chlorine dioxide bleaching process. The advantages of the reduced loss of chlorine dioxide are a very significant reduction in the cost of the wood pulp bleaching process as well as the reduction of pollution levels.

In accordance with the present invention there is provided a bleaching process for bleaching wood pulp in the D_1 or D_2 bleaching stage in an aqueous suspension using chlorine dioxide and providing high brightness and a high brightness ceiling, characterised by the steps of:

subjecting said aqueous wood pulp suspension to a first bleaching step during the D_1 or D_2 bleaching stage by mixing it with chlorine dioxide and/or alkali for about 5-40 minutes so that the pH at the end of said first bleaching step is between about 6.0-10.0;

decreasing the pH of the mixture after said first bleaching step; and

subjecting said mixture to a second bleaching step during the D_1 and/or D_2 bleaching stage for about 2 or more hours so that the pH at the end of the second step is between about 1.9-4.2.

Further aspects of the bleaching process of the present invention are set forth in the accompanying claims, to which reference should now be made.

It is an object of the present invention to provide more efficient chlorine dioxide bleaching in the wood pulp bleaching process.

It is another object of the present invention to significantly reduce the conversion of chlorine dioxide to non-bleaching chemicals during the wood pulp bleaching process.

It is still another object of the present invention to reduce the cost of the wood pulp bleaching process.

It is yet another object of the present invention to achieve a higher wood pulp brightness with a selected chlorine dioxide charge than has heretofore been possible.

Description of the Drawings

Some of the objects having been stated, other objects will become evident as the description proceeds, when taken in connection with the accompanying drawings, in which:

Figure 1 is a graph of the effect of pH on chlorate and chlorite formation in chlorine dioxide bleaching of kraft pulp (reprinted from "The Bleaching of Pulp", Ed. R. P. Singh, p. 137);

Figure 2 is a graph of D_1 brightness for the pulp of Figure 2 when the D_1 charge is varied on the pulp for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 3 is a graph of D_2 brightness versus chlorine dioxide charge for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention wherein the D_2 charge is 0.2% ClO_2 on pulp;

Figure 4 is a graph of D_1 and D_2 brightness versus chlorine dioxide charge for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 5 is a graph of D_1 brightness versus percentage (%) chlorine dioxide on the pulp (D_1 charge) for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 6 is a graph of D_2 brightness for the pulp of Figure 5 when the D_2 charge is 0.2% chlorine dioxide on the pulp for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 6(a) is a graph of final brightness versus ClO_2 charge for the conventional one-step process and the novel two-step bleaching process of the present invention using a (CD) (EO)D sequence. Reverted brightness is also shown after 24 hours at 105°C;

Figure 7 is a graph of D_1 viscosity versus D_1 pH for the conventional one-step bleaching process and high pH for the novel two-step bleaching process of the present invention;

Figure 8 is a graph of total organic chlorine (TOCl) or (AOX) in D_1 plus E_2 effluents versus chlorine dioxide charge in D_1 for the conventional one-step bleaching process and the novel two-step bleaching process of the present invention;

Figure 9 is a graph of chlorate formed in the D_1 stage versus end pH;

Figure 10 is a graph of chlorate formed versus D_1 charge and CE kappa number for conventional bleaching;

Figure 11 is a graph of chlorate formed versus D_1 charge and CE kappa number for the novel two-step high/low pH bleaching process of the present invention;

Figure 12 is a graph of chlorate formed as a percentage (%) of chlorine dioxide converted to chlorate versus percent (%) chlorine dioxide in D_1 for the conventional one-step bleaching process and the novel two-step high/low bleaching process of the present invention;

Figure 13 is a graph of D_1 pulp brightness versus the percentage of chlorine dioxide on the pulp (D_1 charge) for the conventional one-step bleaching process and the novel two-step high/low pH bleaching process of the present invention (wherein the middle line is the calculated brightness due to reduced chlorate formation);

Figure 14 is a graph of chlorate formation versus D_1 brightness for the conventional one-step bleaching process and the novel two-step high/low pH bleaching process of the present invention; and

Figure 15 is a schematic representation of two (2) different process systems for a wood pulp bleaching plant for incorporating the two-step high/low pH bleaching process of the present invention.

Best Mode for Carrying Out the Invention

Chlorine dioxide bleaching of kraft pulps is typically carried out at an end pH of 3.8 for 3 hours at 70° centigrade. It is commonly known that pH has an important bearing on brightness and strength properties as well as the chemical species present in the mixture. As shown in Figure 1 of the drawings, the formation of chlorate increases as the pH of the solution is decreased. Below pH 5 a major loss of oxidizing power occurs since the chlorate formed is inactive as a bleaching agent. Conversely, as the pH is increased, the conversion of chlorine dioxide to the chlorite anion is increased which is also inactive toward lignin. The sum of chlorite plus chlorate is lowest at end pH 3.8 which is found to be optimal for chlorine dioxide bleaching. However, formation of chlorite is not actually lost oxidizing capability since acidifying the chlorite solution forms chlorous acid which is known to be very reactive toward lignin.

In order to increase the efficiency of chlorine dioxide bleaching, a new two-step process has been discovered. The process is as follows:

1. Pulp is mixed with sodium hydroxide and subsequently mixed with chlorine dioxide in a conventional manner. The pH is maintained between about 6 and 7.5 for optimum brightness and viscosity although beneficial results are also found in a pH range of about 5-10. Reaction time is varied between about 5-40 minutes, and the reaction temperature is between about 55-85° centigrade, most suitably about 70° centigrade.

2. After the initial bleaching step, the pulp mixture is acidified to an optimum end pH of 3.8 with sulfuric acid, hydrochloric acid, or other suitable acid. Although a pH of 3.8 is optimal for brightness, end pH values of 1.9-4.2 have been recorded with substantial brightness gains over conventional bleaching methods. Final consistency of the pulp is between about 3-12%, most suitably about 10%, and reaction time in this second step is 2 or more hours, most suitably between about 2.5 and 3.9 hours. Reaction temperature is between about 55-85° centigrade, and most suitably about 70° centigrade.

To prove the efficacy of the new process generally described above, detailed bleaching experiments were carried out by applicant on southern pine kraft pulp. The furnish was obtained from the decker before the bleach plant, and to insure maximum mixing CD stage bleaching was done in plastic Nalgene bottles which rolled on a ball-mill type apparatus for the full reaction time. All other bleaching stages were carried out in sealed polyester bags which were kneaded at various times throughout the bleach to insure proper mixing.

Processing parameters used by applicants for the multiple bleaching stages are listed in Table 1 below. Chlorination stage charges were varied to achieve target (CD)E kappa numbers, and all charges are on OD brownstock pulp. Optimum high/low pH values are 6-7.5 and 3.8, respectively. Large batches of (CD)E pulp were made and then divided into individual DED runs for comparison. All comparisons were made on pulps from the same (CD)E batch, and all water used in bleaching and washing was distilled. Chlorine dioxide solutions used in testing were generated on site by acidifying sodium chlorite solution and absorbing the ClO_2 gas in cold distilled water. Chlorine content in the solutions was kept between 7 and 10% (active basis).

Processing parameters for the bleaching experiments and the analytical methods used in the experiments are as follows:

TABLE 1

Stage	Charge	Time	Temperature	Consistency	End pH
CD	.17-.22 x Kappa % Available Chlorine on Pulp (10% ClO_2 Substitution)	1 hour	30-40° C	3%	<1.8
E_1	0.7 x Cl_2 % Of Caustic on Pulp	1 hour	70° C	10%	>11.5
D_1	varied	3 hours	70° C	10%	3-4
H/L D_1	varied	5-15 mins.	70° C	10.5-13%	5-10
		2.75-2.9 hrs.	70° C	10%	1-9-4.2
E_2	0.75%	1 hour	70° C	10%	>11.5
D_2	varied	3 hours	70° C	10%	3.5-3.8

BRIGHTNESS	Elrepho 2000 ISO
VISCOSITY	TAPPI T230 os-76
KAPPA NUMBER	TAPPI T236 hm-85
TOCl (AOX)	EPA method 9020
CHLORATE	Ion Chromatography

Brightness

On the basis of the results achieved in the bleaching tests, a substantial increase in brightness is always found using the high/low pH bleaching method as compared to conventional bleaching methods. As seen in Figure 2, the D_1 brightnesses achieved were higher than those of the present ClO_2 bleaching techniques. In Figure 2, high pH values are between 8 and 9.5, and low pH values are from 1.9-2.1. The control had end pH values of 3.3 to 3.7. At a brightness level of 76 ISO, a charge of 0.9% ClO_2 on OD pulp was needed for conventional bleaching while only 0.68% was needed using the high/low bleaching method. This accounts for a 24% savings in chlorine dioxide. In 5-stage (CD) (EO)DED bleaching, however, the effect of the brightness gain is reduced in the final bleaching stage (D_2). This is shown in Figure 3, where the pulps of Figure 2 are further bleached in the E_2 and D_2 stages wherein the D_2 stages are run conventionally. After the final bleaching stage, a 15% savings in chlorine dioxide is realized at a brightness of 88.3 ISO.

Regardless of the incoming (CD)E kappa number (lignin concentration), chlorine dioxide savings are always found using the high/low pH bleaching process. This is illustrated in Figure 4 for pulp with a (CD)E kappa number of 8.5. Again a savings of approximately 0.2% ClO_2 on pulp is realized in the D_1 stage, and the magnitude of savings is lower at a comparable D_2 brightness. Thus, even at high (CD)E kappa values, substantial reductions in chlorine dioxide use are realized by the bleaching method of the invention.

Similar brightness ceilings are reached in the D_1 stage irrespective of which method of bleaching is used. This occurs around 84.0 ISO for both methods for an incoming (CD)E kappa of 4.4 (see Figure 5). In Figure 6, D_2 pulp from Figure 5 was found to have an 11% savings in chlorine dioxide even at a very high brightness of 90.5 ISO, but eventually the ceiling is reached at 91.4 ISO at a total charge of 1.2% ClO_2 on OD pulp.

One of the major applications of the novel high/low pH bleaching process is in a three stage sequence (see Figure 6(a)). Current trends toward reducing operational and capital costs of pulp mills have led to the development of short sequence technologies in the pulp and paper industry. The major three-stage sequences are (CD) (EO)D and (CD) (EOP)D, and with high/low pH bleaching it is possible to decrease chlorine dioxide usage by as much as 29% in these processes.

Pulp Viscosity

Pulp viscosity measurements were made using TAPPI standard T 230 os-76. Earlier experimental work has indicated that chlorine dioxide at a pH of less than 5 reacts selectively with lignin, and at a pH greater than 7 chlorine dioxide reacts with the carbohydrate and lignin in the pulp vigorously, which in turn degrades the cellulose chain. As shown in Figure 7, pulp viscosity depends heavily on the pH of the reacting mixture. Pulp viscosity decreases slowly from pH 6 to 7, then falls rapidly at pH values higher than 7. The decrease in viscosity at the high pH for the two-step high/low pH bleaching process is not significant because of the low reaction time in the high pH step. From viscosity and brightness data obtained, a pH of 6-7.5 and a pH of 3.8 is optimal for the high pH and low pH, respectively, in the two-step high/low pH bleaching process.

Table 2 below gives an example of pulp qualities measured from a bleach run performed on a pulp of (CD)E kappa = 4.4 and viscosity 25 cp. An average viscosity drop of 0.6 centipoise was detected for the two-step high/low pH bleaching process as compared to conventional bleaching results. Other bleach runs performed showed a similar effect.

TABLE 2

CONVENTIONAL BLEACHING				
Charge	End pH	CED Bright ISO	(CD)EDED Bright ISO	Viscosity CP
0.4%	3.6	60.2	86.0	24.8
0.6%	3.4	70.5	89.2	24.7
0.8%	3.4	78.3	90.4	24.7
1.0%	3.5	84.6	91.4	24.5

HIGH/LOW pH BLEACHING					
Charge	High pH	Low pH	CED Bright ISO	(CD)EDED Bright ISO	Viscosity CP
0.4%	7.2	3.8	67.5	87.6	24.5
0.6%	7.1	3.7	78.5	89.9	24.1
0.8%	6.7	3.2	82.2	90.9	24.0
1.0%	7.0	3.0	84.5	91.4	24.1

Total Organic Chlorine (TOCl) or (AOX)

TOCl (AOX) measurements in applicant's tests were made on both the D_1 and E_2 for one data set. The values were added together and are shown in Figure 8 of the drawings. Surprisingly, conventional bleaching TOCl values were parabolic versus an increasing ClO_2 charge while TOCl values with the high/low pH bleaching method varied only slightly. A greater decrease in TOCl from bleaching with the two-step high/low pH bleaching process can be realized by substituting the chlorine dioxide saved in the D_1 stage back into the chlorination stage (CD) of the multi-stage bleach sequence. This would result in a decrease in TOCl (AOX) in effluents from the bleach plant.

Chlorate

Chlorate (ClO_3^-) is a well known herbicide, and discharge of chlorate from paper mills has been gaining more attention from environmentalists now that possible detrimental effects on various microalgaes have been observed. Thus, improving the efficiency of chlorine dioxide bleaching by lowering chlorate production may have a favorable impact on both economic and environmental issues. Conversion of chlorine dioxide to chlorate can be lowered by the two-stage high/low pH bleaching method for most chemical charges on pulp. At very high chemical charges (or lower lignin concentrations), chlorate formation is independent of whether the new or conventional bleaching method is used, because a brightness ceiling is reached.

Thus, it is important to determine if the chlorine dioxide saved using the two-step high/low pH bleaching process is due to a subsequent decrease in the formation of chlorate. The two possible pathways of forming chlorate are set forth in Equations 1 and 2 below:

$$\text{Equation 1} \qquad 2ClO_2 + 2OH^- \text{---->} ClO_3^- + ClO_2^- + H_2O$$

$$\text{Equation 2} \qquad 2HClO_2 \text{---->} H^+ + HClO + ClO_3^-$$

Equation 1 is not a very prominent reaction in bleaching carried out at pH 7 since only a small concentration of hydroxyl ions are present. Under typical bleaching conditions, the pH starts around 5 and drops to less than 4 by the end of the bleaching process. At pH 5, less than 1% hydroxyl ions would be present for reaction, and at pH 4 only 0.1% exist. Supporting evidence for this observation is shown in Figure 9 of the drawings. The trend indicated shows that as the pH is increased up to 9, the formation of chlorate decreases.

The major pathway for chlorate formation is Equation 2 above. In principle, chlorous acid reacts with itself to form chlorate and hypochlorous acid. This is a biomolecular reaction which is considered to be slow at low concentrations. Chlorous acid, as stated above, is very reactive toward lignin. Chlorous acid oxidizes lignin and is reduced to hypochlorous acid according to Equation 3:

$$\text{Equation 3} \qquad HClO_2 + \text{LIGNIN} \text{--->} HClO + \text{OXIDIZED LIGNIN}$$

During chlorine dioxide bleaching, a competitive pathway is present for consumption of chlorous acid. A high chemical charge would increase the rate of reaction of Equation 2, and a high lignin concentration would increase the rate of reaction of Equation 3. Figure 10 shows a plot of D_1 charge of chlorine dioxide versus % chlorine dioxide converted to chlorate for conventional chlorine dioxide bleaching. As the lignin concentration is increased (low chemical charge or higher kappa number) less chlorate is formed. Likewise if a high concentration of chemical is present (low kappa number), the higher the formation of chlorate. The same trend also holds true for the two-step high/low pH bleaching process as can be seen in Figure 11. From Figures 10 and 11, it is evident that the two-step high/low pH bleaching process significantly lowers chlorate formation at most chemical charges. However, little difference is seen at high charges where the brightness ceiling is reached.

Corresponding chlorate measurements for the brightness shown in Figure 5 are plotted on Figure 12. Again, as the charge is increased, the formation of chlorate rises. In order to determine the chlorine dioxide savings in terms of chlorate reduction, the chlorate measurements are expressed as available chlorine. At a brightness of 78.3 ISO, the high/low pH bleaching process and conventional bleaching required 0.6% and 0.8% ClO_2 on pulp, respectively. These charges correspond to 1753 parts per million (ppm) and 2338 ppm, respectively, as available chlorine. The difference provides a savings of 585 ppm available chlorine. Chlorate measurements were found to be 351 ppm and 423.3 ppm as available chlorine for the high/low pH bleaching process and normal bleaching, respectively, at a charge of 0.6% on pulp for a 17% reduction. Subtraction yields a savings of 72.3 ppm available chlorine, which corresponds to only 17% of the total savings realized of 423.3 ppm. Figure 13 of the drawings demonstrates this effect by replotting Figure 6 with the calculated savings due to chlorate reduction. It is apparent that a decrease of chlorate is not sufficient to explain the total ClO_2 savings. A change in lignin structure and/or greater solubilization of the lignin may be possible explanations for the total savings in the ClO_2 observed in the tests.

A larger reduction in chlorate is realized at a comparable D_1 brightness. As shown in Figure 14, it is possible to reduce chlorate by as much as 45% (at 78.3 ISO) using the two-step high/low pH bleaching process as compared to a conventional ClO_2 bleaching stage. Chlorate formation in the D_2 stage is identical for either bleaching process since they are carried out identically.

Process Apparatus

The two-step high/low pH bleaching process can be implemented in both a new plant or an existing pulp bleaching plant. The optimum design schematic is shown in Figure 15, where ClO_2 and caustic are added to the first mixer. The pulp flows into a J or U tube (Figure 15A) or upflow tower (Figure 15B) with a retention time of approximately 5-40 minutes. A second mixer is provided to mix the acid for pH adjustment of the wood pulp. The pulp can then be discharged directly to a downflow tower. The retention time in the downflow tower is 2 or more hours and most suitably between about 2.5-3.9 hours. In an existing bleach plant the simplest method for implementing the two-step high/low pH bleaching process technology would be to install a mixer on the discharge from the upflow leg of the tower to the downflow leg of the tower.

Typical chemical charges for conventional bleaching process and high/low pH bleaching process stages are listed in Table 3 below. The chlorine dioxide savings is 4 lb/ton, while the caustic and the acid charge increase by 3 lb/ton and 3.6 lb/ton, respectively.

TABLE 3

	Conventional Bleaching	High/Low pH Bleaching
Chlorination		
% Chlorine % ClO_2	4.10 .46	4.10 .46
Extraction		
% Caustic CE kappa	3.4 4.4	3.4 4.4
Chlorine Dioxide		
% ClO_2	0.8	0.6
% NaOH	0.55	0.7
% H_2SO_4		0.18
Brightness (ISO)	78.3	78.5

The following conclusions can be drawn about the novel 2-step high/low pH bleaching process described herein from the bleaching of mill southern pine kraft pulps:

1. The high/low pH bleaching process reduces chlorine dioxide usage by as much as 24% in the D_1 stage;

2. The formation of chlorinated organic material characterized by TOCl can be decreased by the use of the high/low pH bleaching process if the ClO_2 saved is substituted into the CD stage;

3. The formation of chlorate is decreased by as much as 45% in the D_1 stage using the high/low pH bleaching process at a target D_1 brightness;

4. The high/low pH bleaching process can be easily implemented in either a new mill or an existing mill; and

5. The formation of chlorate at acidic bleaching conditions is due to the biomolecular reaction of chlorous acid with itself. Formation of chlorate can be reduced by lower bleach chemical charges or higher kappa number pulps.

It will be understood that various details of the invention may be changed without departing from the scope of the invention. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation--the invention being defined by the claims.

Claims

1. A bleaching process for bleaching wood pulp in the D_1 or D_2 bleaching stage in an aqueous suspension using chlorine dioxide and providing high brightness and a high brightness ceiling, characterised by the steps of:

   subjecting said aqueous wood pulp suspension to a first bleaching step during the D_1 or D_2 bleaching stage by mixing it with chlorine dioxide and/or alkali for about 5-40 minutes so that the pH at the end of said first bleaching step is between about 6.0-10.0;
   decreasing the pH of the mixture after said first bleaching step; and
   subjecting said mixture to a second bleaching step during the D_1 and/or D_2 bleaching stage for about 2 or more hours so that the pH at the end of the second step is between about 1.9-4.2.

2. A bleaching process according to claim 1 wherein, in the said first bleaching step, the wood pulp suspension is mixed with alkali and 10% to 50% of the total chlorine dioxide charge, the remaining chlorine dioxide charge being added for the second bleaching step.

3. A bleaching process according to claim 1 or 2, wherein said alkali comprises sodium hydroxide.

4. A bleaching process according to any preceding claim, wherein the end pH of the mixture during said first bleaching step is between about 6.0-7.5.

5. A bleaching process according to any preceding claim, wherein the temperature during said first bleaching step is between about 50-85°C.

6. A bleaching process according to claim 5, wherein the temperature during said first bleaching step is about 70°C.

7. A bleaching process according to any preceding claim, wherein the end pH of the mixture during said second bleaching step is about 3.8.

8. A bleaching process according to any preceding claim, wherein the temperature during said second bleaching step is about 55-85°C.

9. A bleaching process according to claim 8, wherein the temperature during said second bleaching step is about 70°C.

10. A bleaching process according to any preceding claim, wherein the final consistency of the mixture after said second bleaching step is between about 3-12%.

11. A bleaching process according to claim 10, wherein the final consistency of the mixture after said second bleaching step is about 10%.

12. A bleaching process according to any preceding claim, wherein the duration of the second bleaching step is about 2.5 to 3.9 hours.

13. A bleaching process according to any preceding claim, wherein the pH is decreased with an acid.

14. A bleaching process according to claim 13, wherein said acid is selected from the group consisting of sulphuric acid and hydrochloric acid.

15. A bleaching process according to any preceding claim, where said bleaching process is used in a three stage sequence process.

16. A bleaching process according to claim 15, wherein said bleaching process is used in the first chlorine dioxide bleaching stage in a five stage sequence process.

17. A bleaching process according to claim 16, wherein the five stage sequence process is a $(CD)(EO)D_1E_2D_2$ process and the first bleaching stage is followed by conventional extraction and bleaching stages.

Patentansprüche

1. Bleichverfahren zum Bleichen von Zellstoff in der D_1- oder D_2-Bleichstufe in einer wäßrigen Suspension unter Verwendung von Chlordioxid, wobei ein hoher Weißgrad und eine hohe Weißgrad-Grenze erreicht werden,gekennzeichnet durch die folgenden Schritte:

   - die wäßrige Zellstoffsuspension wird einem ersten Bleichschritt während der D_1- oder D_2-Bleichstufe unterworfen, indem sie mit Chlordioxid und/oder Alkali während etwa 5 bis 40 Minuten gemischt wird so daß der pH am Ende des ersten Bleichschritts zwischen etwa 6,0 und 10,0 liegt.
   - der pH der Mischung wird nach dem ersten Bleichschritt verringert; und
   - die Mischung wird während der D_1- und/oder D_2-Bleichstufe einem zweiten Bleichschritt während etwa zwei oder mehr Stunden unterworfen, so daß der pH am Ende des zweiten Schritts zwischen etwa 1,9 und 4,2 liegt.

2. Bleichverfahren nach Anspruch 1, worin im ersten Bleichschritt die Zellstoffsuspension mit Alkali und 10% bis 50% der gesamten Chlordioxid-Zugabe gemischt wird und die restliche Chlordioxid-Zugabe beim zweiten Bleichschritt zugegeben wird.

3. Bleichverfahren nach Anspruch 1 oder 2, worin das Alkali Natriumhydroxid enthält.

4. Bleichverfahren nach einem der vorangehenden Ansprüche, worin der End-pH-Wert des Gemisches während des ersten Bleichschritts zwischen etwa 6,0 und 7,5 liegt.

5. Bleichverfahren nach einem der vorangehenden Ansprüche, worin die Temperatur während des ersten Bleichschritts zwischen etwa 50 und 85°C liegt.

6. Bleichverfahren nach Anspruch 5, worin die Temperatur während des ersten Bleichschritts etwa 50°C beträgt.

7. Bleichverfahren nach einem der vorangehenden Ansprüche, worin der End-pH-Wert der Gemisches während des zweiten Bleichschrittes etwa 3,8 ist.

8. Bleichverfahren nach einem der vorangehenden Ansprüche, worin die Temperatur während des zweiten Bleichschritts etwa 55 bis 85°C ist.

9. Bleichverfahren nach Anspruch 8, worin die Temperatur während des zweiten Bleichschritts etwa 70°C ist.

10. Bleichverfahren nach einem der vorangehenden Ansprüche, worin die End-Konsistenz des Gemisches nach dem zweiten Bleichschritt zwischen etwa 3 und 12% liegt.

11. Bleichverfahren nach Anspruch 10, worin die End-Konsistenz des Gemisches nach dem zweiten Bleichschritt etwa 10 % ist.

12. Bleichverfahren nach einem der vorangehenden Ansprüche, worin die Dauer des zweiten Bleichschritts etwa 2,5 bis 3,9 Stunden ist.

13. Bleichverfahren nach einem der vorangehenden Ansprüche, worin der pH-Wert mit einer Säure herabgesetzt wird.

14. Bleichverfahren nach Anspruch 13, worin die Säure ausgewählt ist aus der Gruppe Schwefelsäure und Chlorwasserstoffsäure.

15. Bleichverfahren nach einem der vorangehenden Ansprüche, worin das Bleichverfahren in einem Drei-Stufen-Sequenzverfahren verwendet wird.

16. Bleichverfahren nach Anspruch 15, worin das Bleichverfahren in der ersten Chlordioxid-Bleichstufe in einem Fünf-Stufen-Sequenzverfahren verwendet wird.

17. Bleichverfahren nach Anspruch 16, worin das Fünf-Stufen-Sequenzverfahren ein (CD), (EO), $D_1E_2D_2$-Verfahren ist und auf die erste Bleichstufe die üblichen Extraktions- und Bleichstufen folgen.

Revendications

1. Procédé de blanchiment, pour blanchir la pâte de bois à l'étape de blanchiment D_1 ou D_2, dans une suspension aqueuse, en employant le dioxyde de chlore et en fournissant une brillance élevée et un plafond de haute brillance, caractérisé par les étapes qui consistent à :

   - soumettre ladite suspension aqueuse de pâte à bois à une première étape de blanchiment durant le stade de blanchiment D_1 ou D_2 en la mélangeant avec du dioxyde de chlore et/ou de l'alcali pendant environ 5 à 40 minutes, de façon à ce que le pH à la fin de ladite première étape de blanchiment soit compris entre environ 6,0-10,0 ;
   - diminuer le pH du mélange après ladite première étape de blanchiment et,
   - soumettre ledit mélange à une seconde étape de blanchiment pendant ladite période de blanchiment D_1 et/ou D_2, pendant environ 2 heures ou davantage de sorte que le pH à la fin de la seconde étape soit compris entre environ 1,9 et 4,2.

2. Procédé de blanchiment selon la revendication 1, caractérisé en ce que, dans ladite première étape de blanchiment, la suspension de pâte de bois est mélangée à de l'alcali et 10 à 50 % de la charge totale en dioxyde de chlore, le restant de la charge en dioxyde de chlore étant ajouté pendant la seconde étape de blanchiment.

3. Procédé de blanchiment selon la revendication 1 ou la revendication 2, caractérisé en ce que ledit alcali compris l'hydroxyde de sodium.

4. Procédé de blanchiment selon chaque revendication précédente, caractérisé en ce que le pH final du mélange pendant ladite première étape de blanchiment est compris entre environ 6,0 et 7,5.

5. Procédé de blanchiment selon l'une des revendications précédentes, caractérisé en ce que la température durant ladite première étape de blanchiment est comprise entre environ 50 et 85°C.

6. Procédé de blanchiment selon la revendication 5, caractérisé en ce que la température durant ladite première étape de blanchiment est environ de 70°C.

7. Procédé de blanchiment selon l'une des revendications précédentes, caractérisé en ce que le pH final du mélange durant ladite seconde étape de blanchiment est environ de 3,8.

8. Procédé de blanchiment selon l'une des revendications précédentes, caractérisé en ce que la température durant ladite seconde étape de blanchiment est environ de 55-85°C.

9. Procédé de blanchiment selon la revendication 8, caractérisé en ce que la température durant ladite seconde étape de blanchiment est environ de 70°C.

10. Procédé de blanchiment selon l'une des revendications précédentes caractérisé en ce que la consistance finale du mélange, après ladite seconde étape de blanchiment est comprise entre environ 3 et 12 %.

11. Procédé de blanchiment selon la revendication 10, caractérisé en ce que la consistance finale du mélange après ladite seconde étape de blanchiment est environ de 10 %.

12. Procédé de blanchiment selon l'une des revendications précédentes, caractérisé en ce que la durée de la seconde étape de blanchiment est comprise entre environ 2,5 et 3,9 heures.

13. Procédé de blanchiment selon l'une des revendications précédentes, caractérisé en ce que le pH est abaissé à l'aide d'un acide .

14. Procédé de blanchiment selon la revendication 13, caractérisé en ce que ledit acide est choisi dans le groupe de l'acide sulfurique et l'acide chlorhydrique.

15. Procédé de blanchiment selon l'une des revendications précédentes, caractérisé en ce que ledit procédé de blanchiment est employé dans un procédé de séquence en trois étapes.

16. Procédé de blanchiment selon la revendication 15, caractérisé en ce que ledit procédé de blanchiment est employé dans le premier stade de blanchiment avec du dioxyde de chlore, dans un procédé de séquence en cinq étapes.

17. Procédé de blanchiment selon la revendication 16, caractérisé en ce que le procédé de séquence en cinq étapes est un procédé (CD) (EO)$D_1E_2D_2$ et que la première étape de blanchiment est suivie d'étapes d'extraction conventionnelle et de blanchiment.

FIG.1

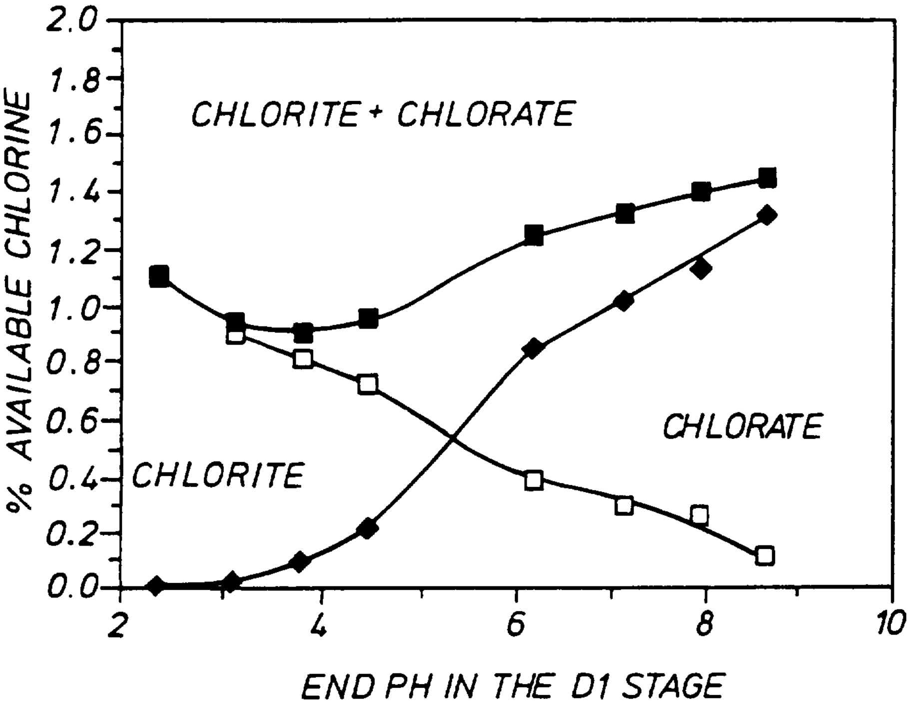

% AVAILABLE CHLORINE
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2
4
6
8
10
END PH IN THE D1 STAGE
CHLORITE + CHLORATE
CHLORATE
CHLORITE

FIG.2

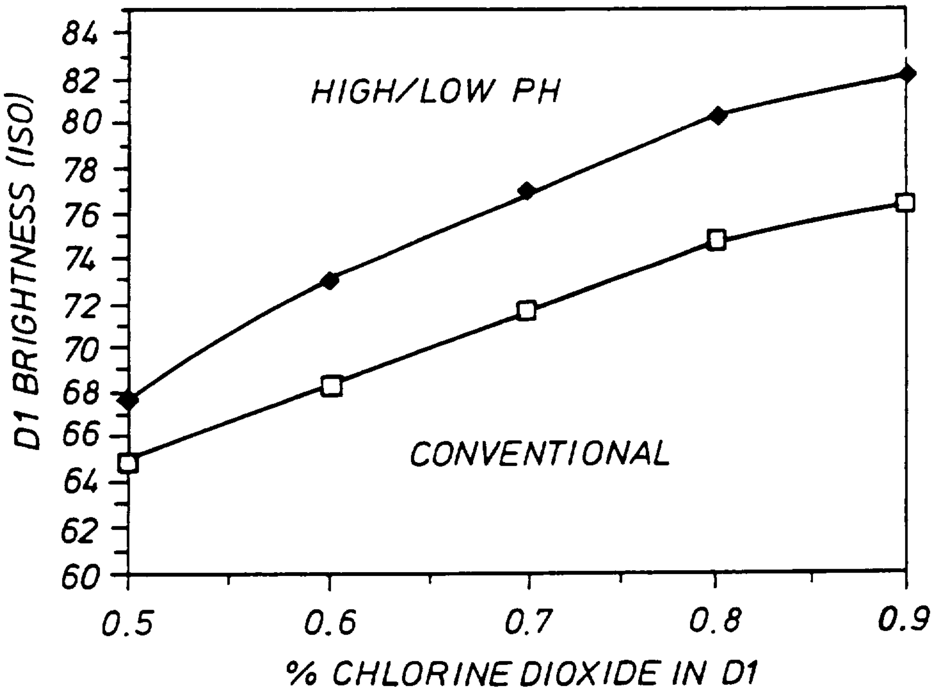

D1 BRIGHTNESS (ISO)
84
82
80
78
76
74
72
70
68
66
64
62
60
0.5
0.6
0.7
0.8
0.9
% CHLORINE DIOXIDE IN D1
HIGH/LOW PH
CONVENTIONAL

FIG.3

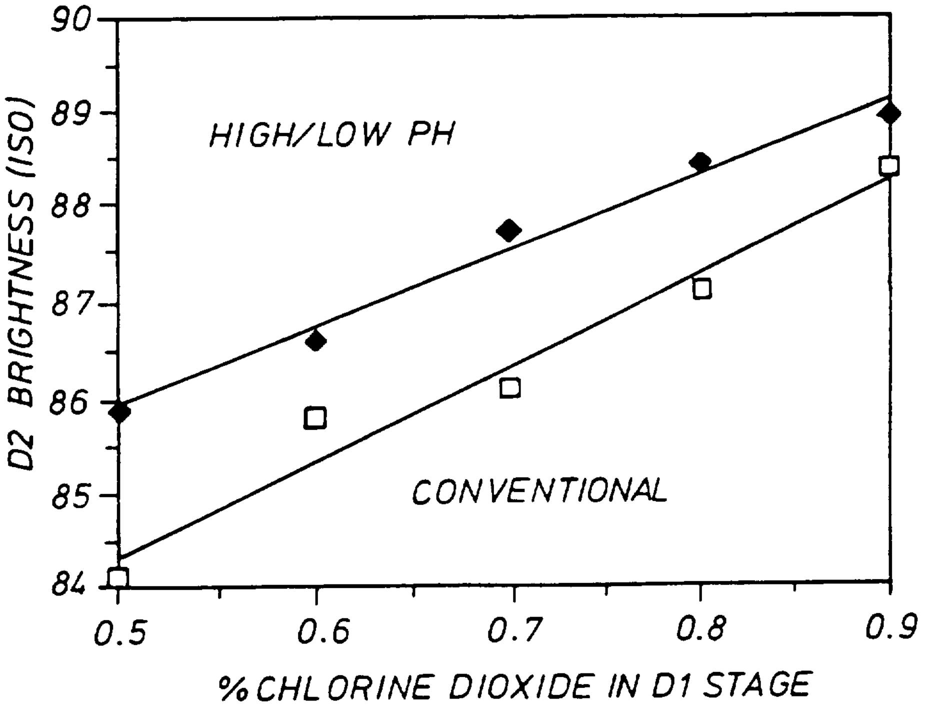

90
89
88
87
86
85
84
D2 BRIGHTNESS (ISO)
HIGH/LOW PH
CONVENTIONAL
0.5
0.6
0.7
0.8
0.9
% CHLORINE DIOXIDE IN D1 STAGE

FIG.4

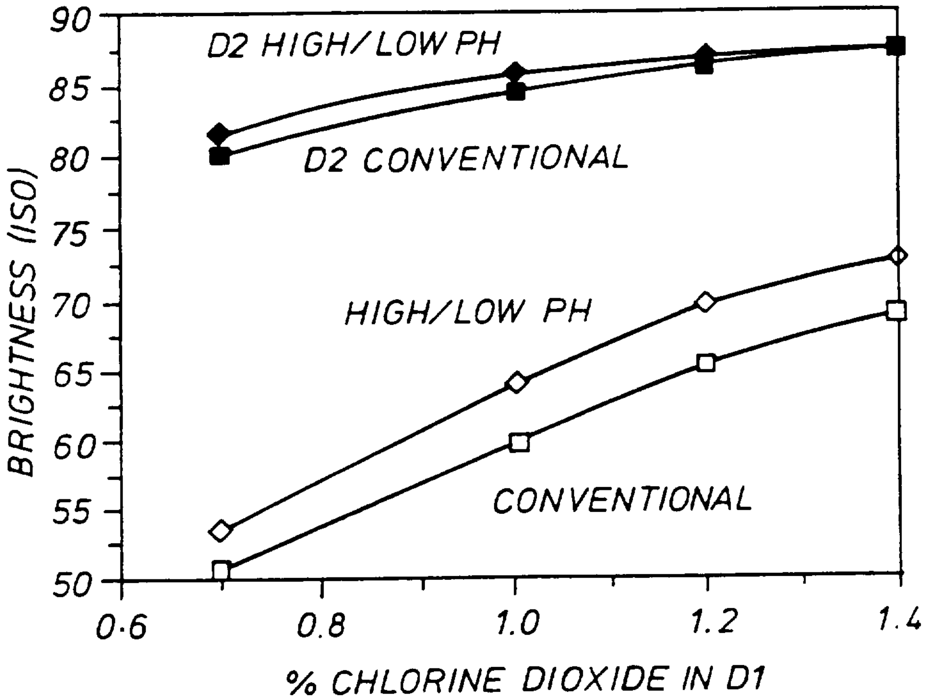

90
85
80
75
70
65
60
55
50
BRIGHTNESS (ISO)
D2 HIGH/LOW PH
D2 CONVENTIONAL
HIGH/LOW PH
CONVENTIONAL
0·6
0.8
1.0
1.2
1.4
% CHLORINE DIOXIDE IN D1

FIG.5

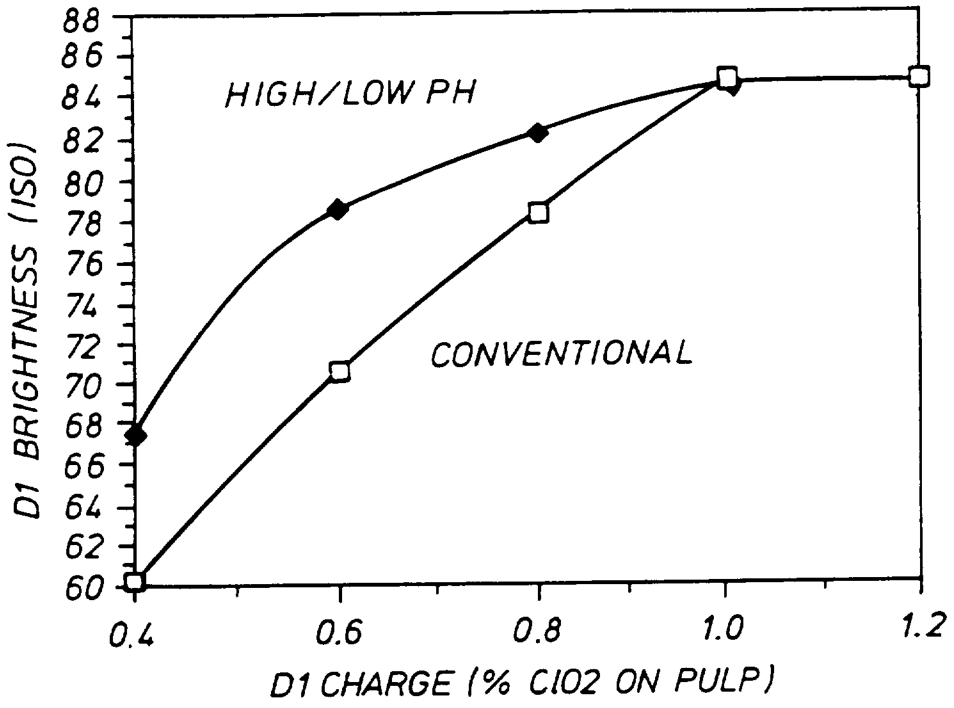
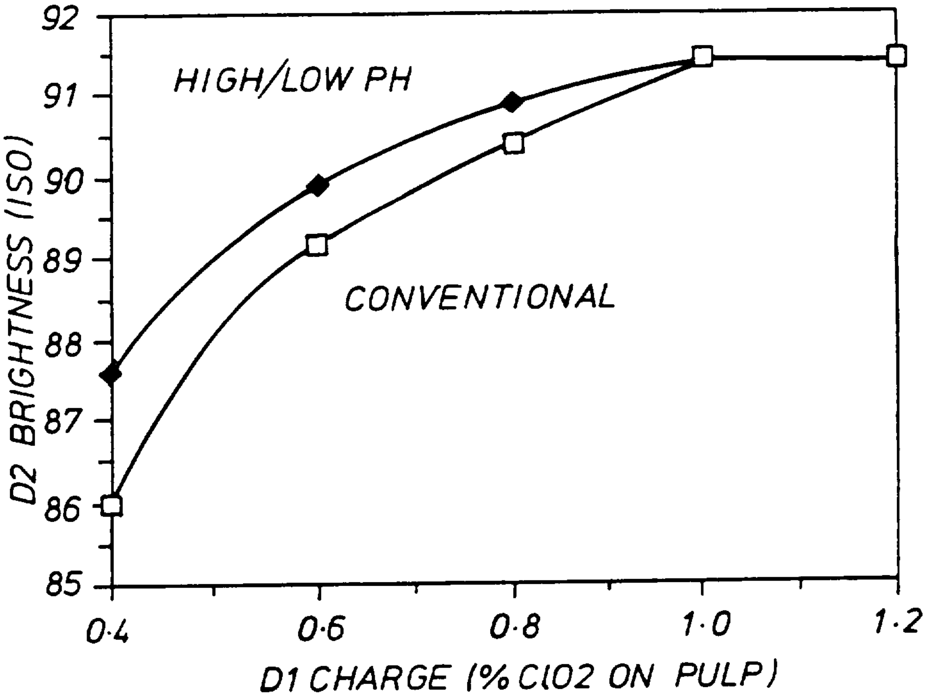
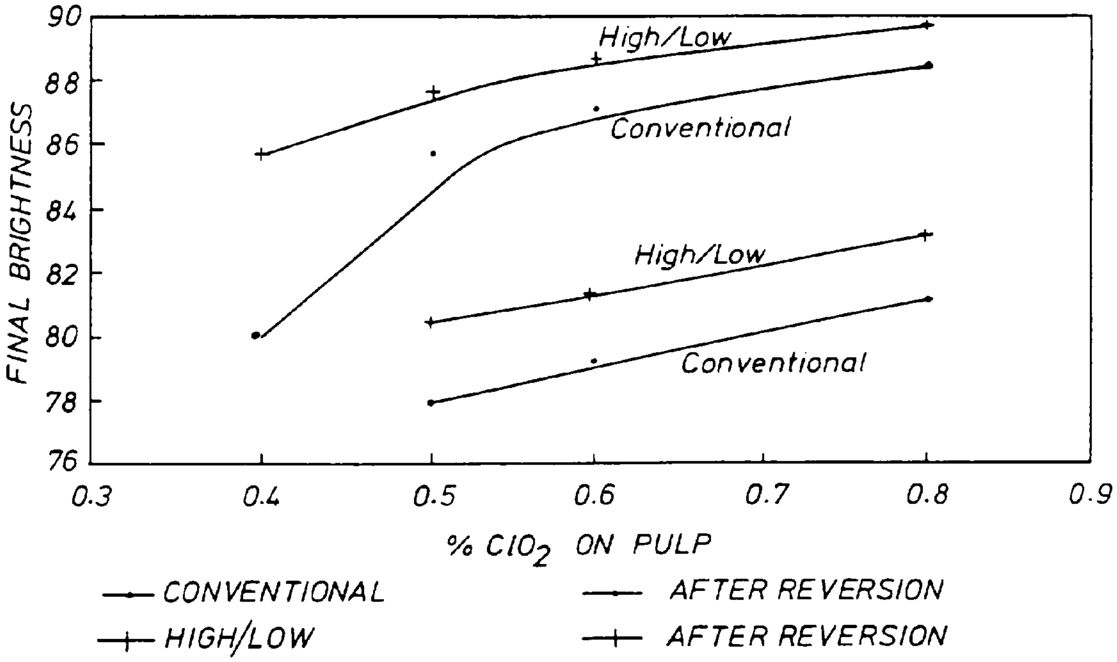

HIGH/LOW PH
CONVENTIONAL
D1 BRIGHTNESS (ISO)
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
0.4
0.6
0.8
1.0
1.2
D1 CHARGE (% ClO2 ON PULP)

FIG.6


HIGH/LOW PH
CONVENTIONAL
D2 BRIGHTNESS (ISO)
92
91
90
89
88
87
86
85
0·4
0·6
0·8
1·0
1·2
D1 CHARGE (% ClO2 ON PULP)



(DC)(EO) Kappa = 2.7 FIG.6a

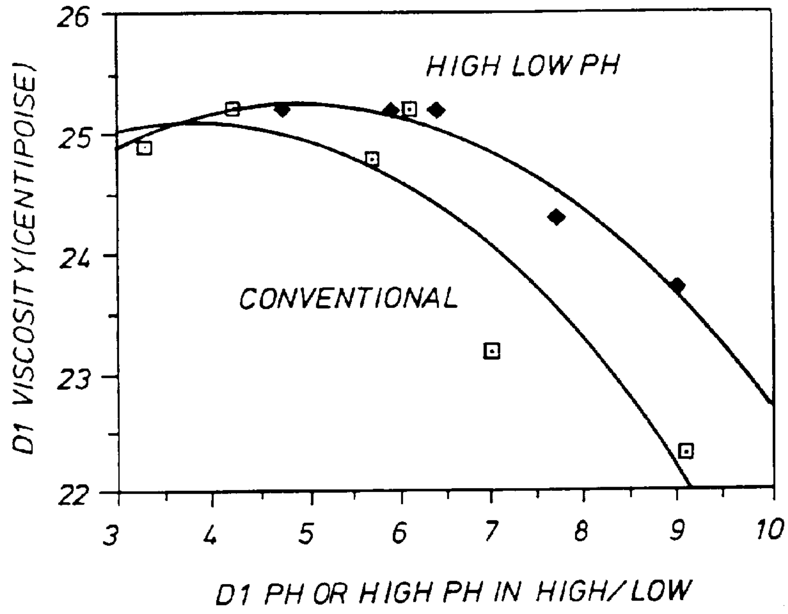


FIG.7

FIG.8

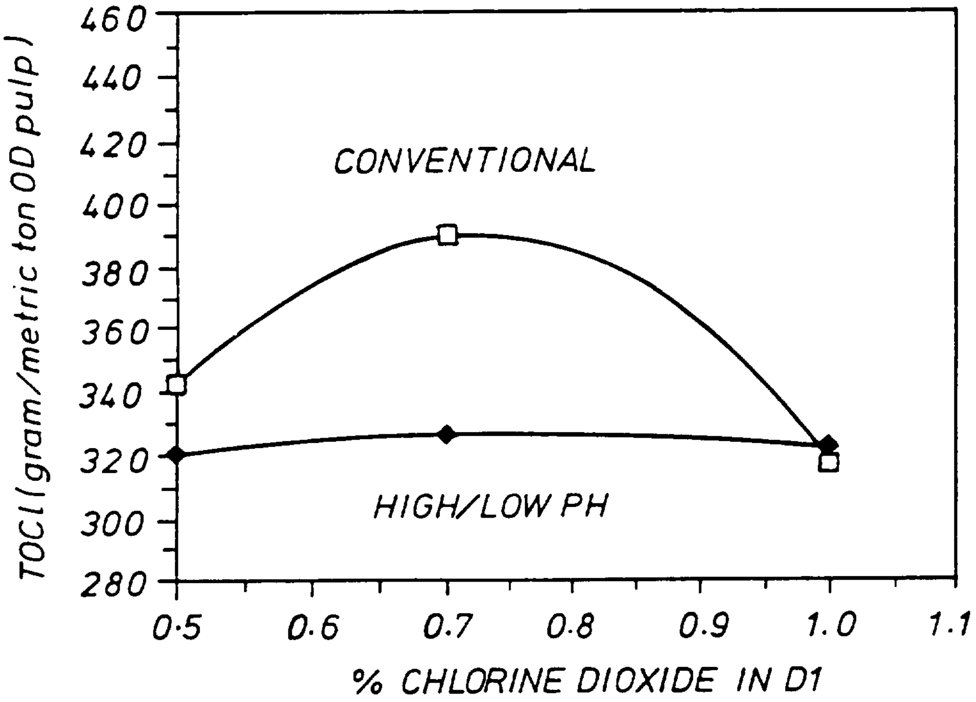

TOCl (gram/metric ton OD pulp)
460
440
420
400
380
360
340
320
300
280
CONVENTIONAL
HIGH/LOW PH
0·5
0·6
0·7
0·8
0·9
1.0
1.1
% CHLORINE DIOXIDE IN D1

FIG.9

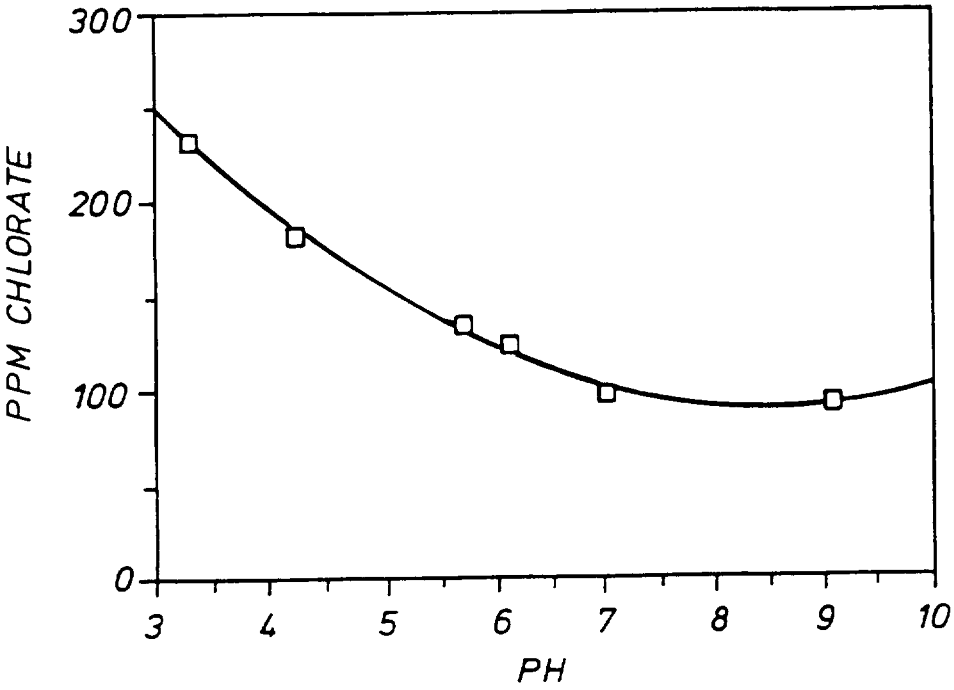

PPM CHLORATE
300
200
100
0
3
4
5
6
7
8
9
10
PH

FIG.10

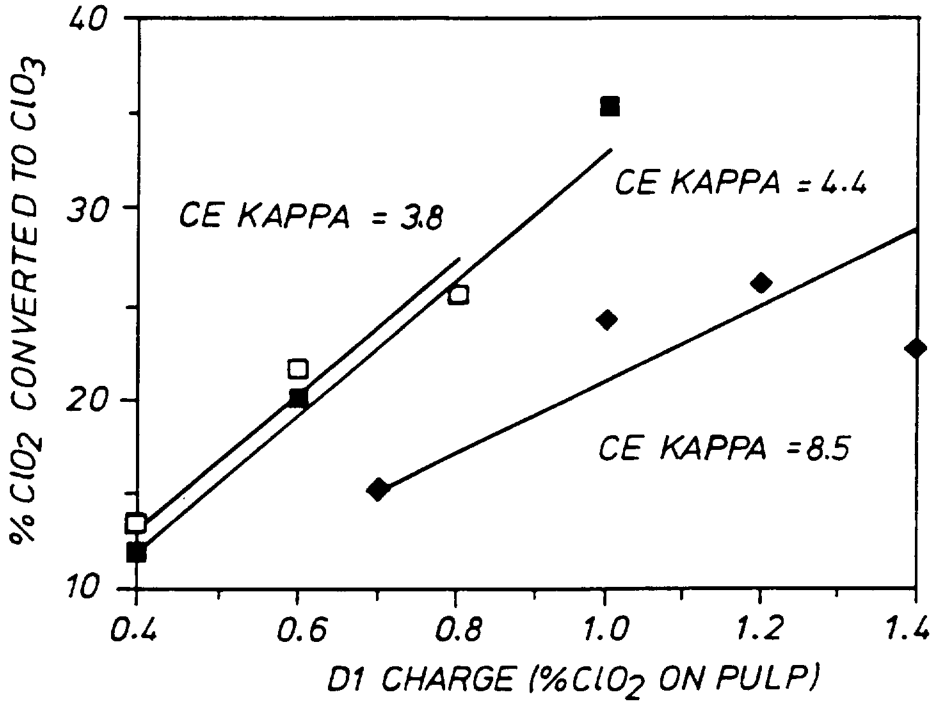

% ClO2 CONVERTED TO ClO3
40
30
20
10
0.4
0.6
0.8
1.0
1.2
1.4
D1 CHARGE (%ClO2 ON PULP)
CE KAPPA = 3.8
CE KAPPA = 4.4
CE KAPPA = 8.5

FIG.11

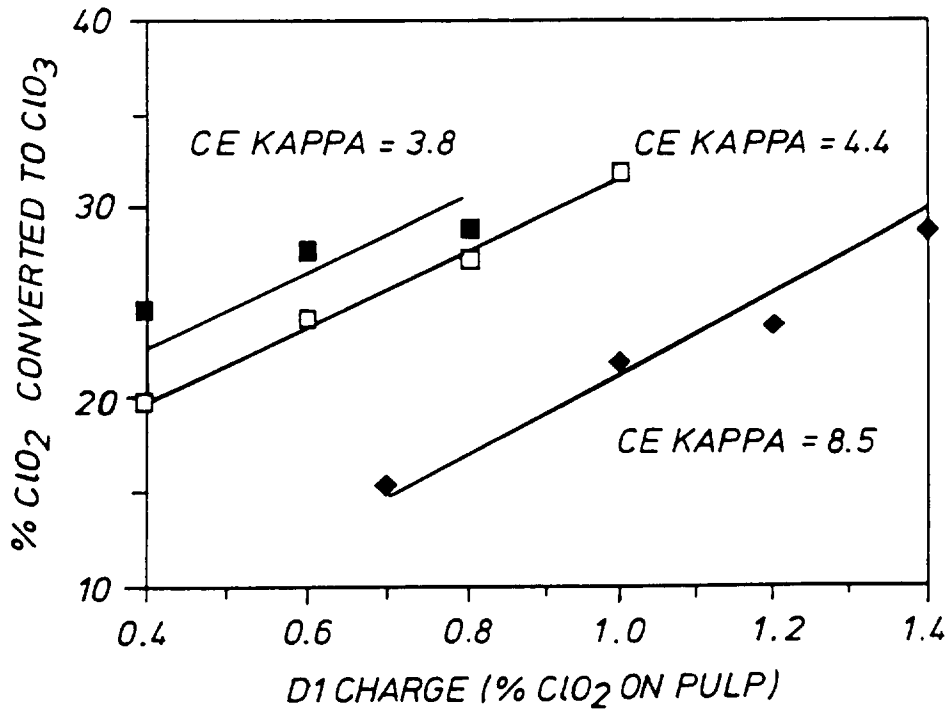

% ClO2 CONVERTED TO ClO3
40
30
20
10
0.4
0.6
0.8
1.0
1.2
1.4
D1 CHARGE (% ClO2 ON PULP)
CE KAPPA = 3.8
CE KAPPA = 4.4
CE KAPPA = 8.5

FIG.12

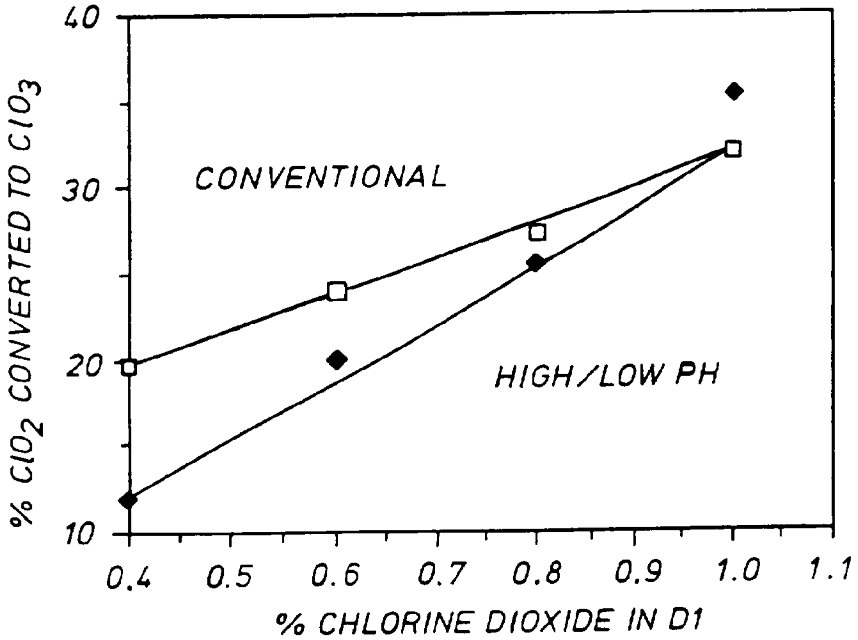

40
30
20
10
% ClO2 CONVERTED TO ClO3
CONVENTIONAL
HIGH/LOW PH
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
% CHLORINE DIOXIDE IN D1

FIG.13

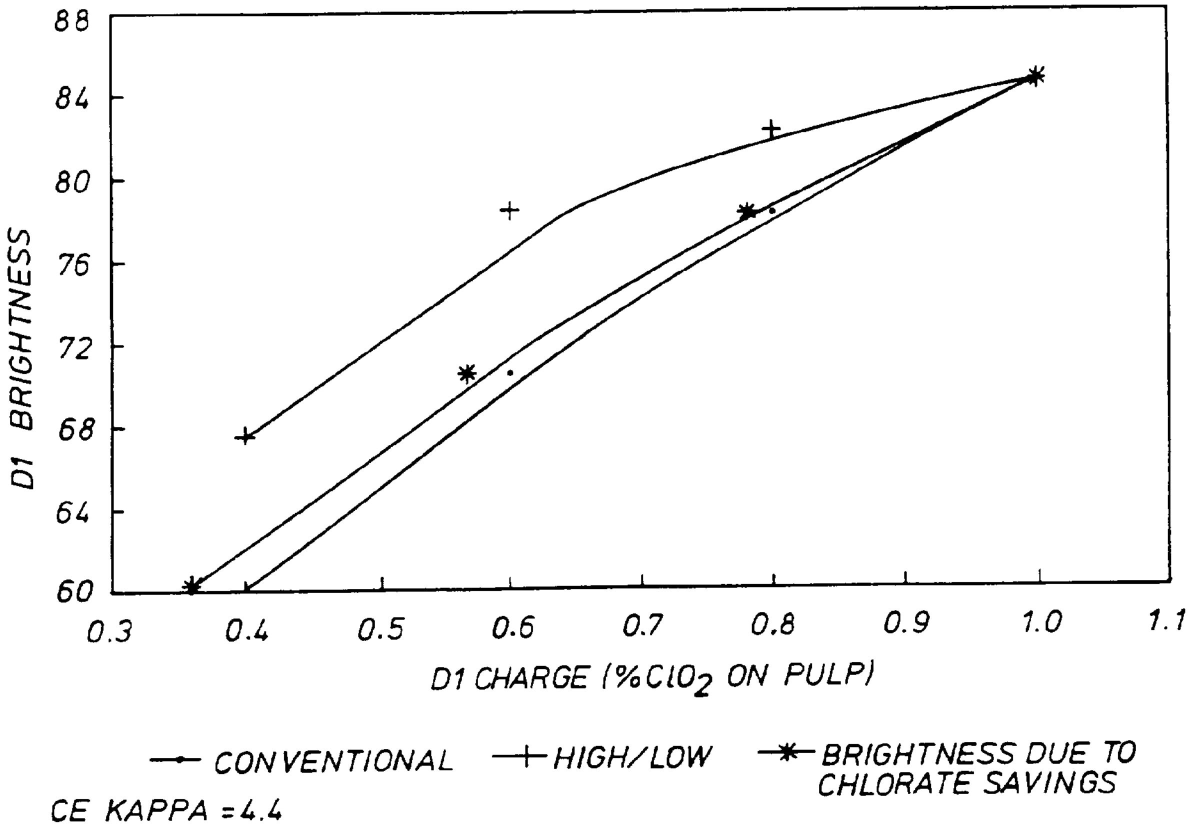
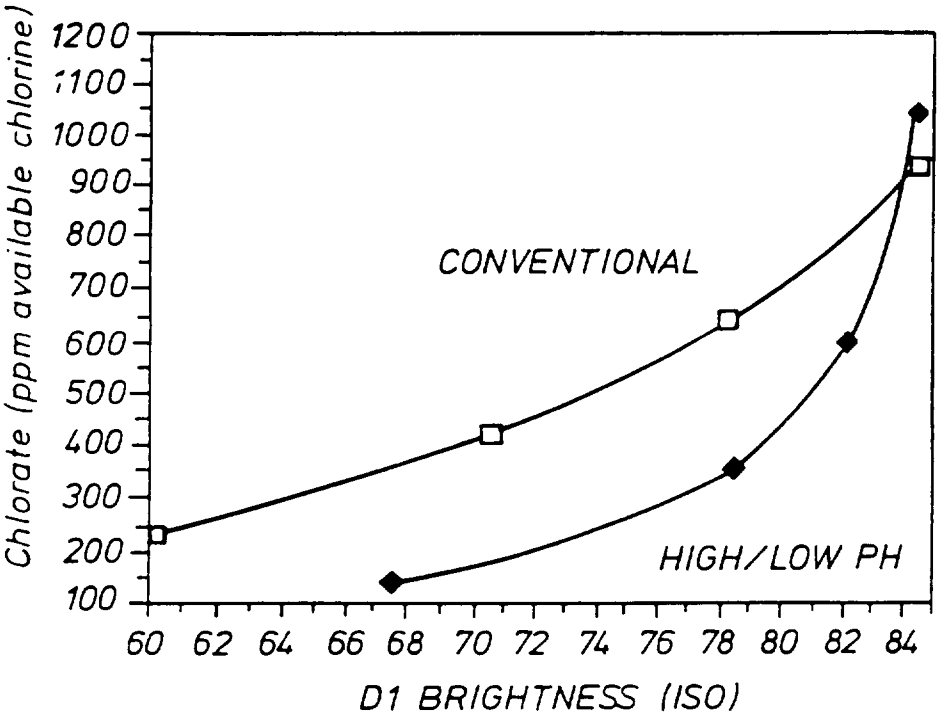

88
84
80
76
72
68
64
60
D1 BRIGHTNESS
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
D1 CHARGE (%ClO2 ON PULP)
CONVENTIONAL
HIGH/LOW
BRIGHTNESS DUE TO CHLORATE SAVINGS
CE KAPPA =4.4

FIG.14.


Chlorate (ppm available chlorine)
1200
1100
1000
900
800
700
600
500
400
300
200
100
60
62
64
66
68
70
72
74
76
78
80
82
84
D1 BRIGHTNESS (ISO)
CONVENTIONAL
HIGH/LOW PH

MILL APPLICATIONS

FIG.15 A

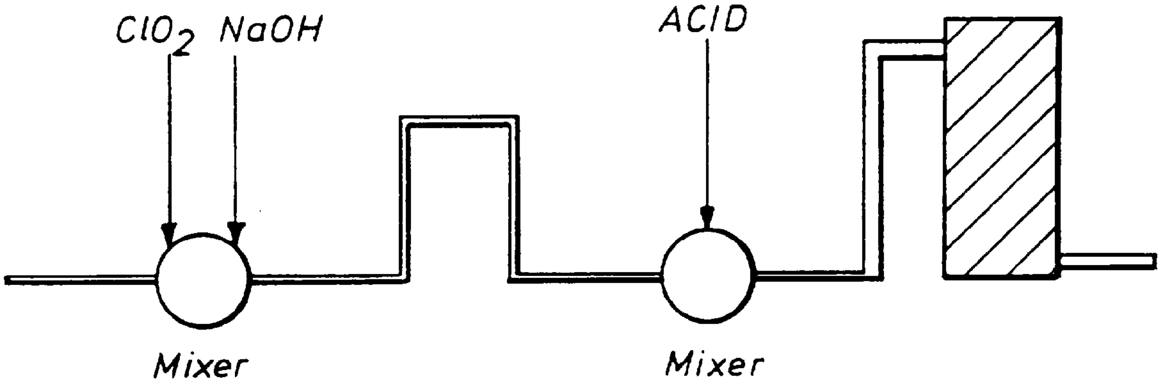


FIG.15B