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54 **Oxygen alkali extraction process for producing bleached pulp.**

57 Oxygen alkali extraction of pulp in a multi-stage bleaching sequence is accomplished in the absence of a dynamic mixer for mixing oxygen with pulp yet obtaining desired pulp brightness and/or reduced chlorine-based chemical consumption, by intimately mixing oxygen with the alkaline pulp at a point before or within the alkaline pulp bleaching stage of the sequence, in the presence of a co-oxidant.

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OXYGEN ALKALI EXTRACTION PROCESS FOR PRODUCING BLEACHED PULP

This Application is a continuation-in-part of United States Patent Application Serial No. 842,349 filed March 21, 1986.

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TECHNICAL FIELD

The present invention is concerned with the manufacture of bleached pulp, particularly for the production of white cellulosic paper products.

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BACKGROUND OF THE INVENTION

15 In the manufacture of bleached pulp the unbleached brown pulp ("brownstock") from the pulp mill is directed to the bleach plant where it is subjected to a series of delignifying/bleaching process steps, each involving distinctly different bleaching chemicals and/or process conditions. Whereas the process objective of pulping is to chemically delignify wood or other ligno-cellulosic 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.

20 Multiple process steps, constituting one bleach "sequence," are used to bleach pulp to the desired brightness level, which usually ranges from 75-93 brightness units (I.S.O), typically greater than 79. Many different sequences have been studied, but some representative, commercially practiced examples are: CEDED, C_DEDED, OCEDED, CEHD, CEHD, OCEH, CEHDED and CHHD.

where:

C = Chlorination with chlorine (Cl₂), sometimes accomplished with coaddition or pretreatment with chlorine dioxide (C_D or D/C).

E = Alkali Extraction with NaOH.

D = Dioxide treatment with chlorine dioxide (ClO₂).

H = Alkaline Hypochlorite bleaching, typically with sodium or calcium hypochlorite (NaOCl or Ca(OCl)₂).

O = Oxygen bleaching with molecular oxygen (O₂).

35 Each sequence can be different not only with respect to the order of chemical addition but also in process configuration.

For example, in a typical CEDED bleach sequence in a displacement bleaching process and also in the common multi-stage process employing a (pulp) downflow or upflow E-stage, the pulp becomes progressively brighter with each bleach step and contains less residual lignin. The actual sequence utilized by a given plant is a reflection not only of target brightness, but also local process economics, feedstock type, end use of the bleached pulp product, and age of mill.

40 In addition to target brightness levels, pulp strength and yield after bleaching are important to the pulp manufacturer. Multistep bleaching utilizing progressively milder and more selective bleaching agents, which tend to be relatively more expensive chemicals, is necessary with the present state-of-the-art to maintain the pulp strength and yield. For example, typical brownstock pulp of 28-35 Kappa can be bleached in a CE sequence (two stage) to a Kappa less than 6; but if one attempted to achieve a brightness level of 88 with this chlorine, the chlorine would begin to react with the cellulosic pulp (modify structure and depolymerize cellulose) reducing both the yield and fiber strength.

45 It is economically and environmentally desirable to develop oxygen-based bleaching technology(ies) that:

1. reduces the number of process steps,
2. reduces consumption of the more expensive bleaching compounds like hypochlorite and chlorine dioxide,
3. reduces the consumption of more cellulose-degrading compounds like chlorine and hypochlorite,
4. increases bleach plant capacity,

5. eliminates/reduces usage of chlorine,
6. reduces bleach plant effluent.

Recently, a relatively new oxygen-based process technology called "Oxygen Alkali Extraction" was commercially introduced into bleach plants that offers considerable economic incentives. Oxygen Alkali Extraction has been symbolized in bleach sequence terminology as E_0 . Although the basic technology is only a few years old, many bleach plants have already commercially adopted the process technology in their respective sequences. Some representative examples are: $C_D E_0 D$, $C_D E_0 H H$, $C_D E_0 D E D$, $C E_0 H$, $C E_0 H D P$, $O C_D E_0 H D$, and $O C_D H E_0 D E H$.

The primary effect of the E_0 process technology is to reduce consumption of chlorine dioxide and hypochlorite in the subsequent bleach stages while retaining pulp brightness and strength. This effect has been utilized to attain a net cost savings benefit among other useful beneficial advantages, such as:

1. Reduction in consumption of chlorine dioxide or hypochlorite (per ton pulp), which are more expensive than oxygen, and environmentally less attractive,
2. Reduction in number of bleach process steps without loss of brightness; e.g., $C E D E D \rightarrow C E_0 D$.
3. Increased bleach plant production rate without additional quantities of chlorine-based chemicals or added bleaching towers.
4. Increased brightness without additional chlorine-based chemicals.
5. Increased pulp viscosity and strength properties by reduction in more cellulose-degrading chemicals like chlorine and hypochlorite.

The subscript terminology generally implies the indicated (subscript) chemical is added to that vessel, e.g., C_D . Notwithstanding the E_0 nomenclature, the oxygen is not added directly to the E-stage vessel/tower.

In present practice of the E_0 stage a dynamic mixer, to which the oxygen is directly added to effect efficient O_2 /pulp mixing, is incorporated between the C- and E-stage vessel/tower. The term "dynamic mixer" is defined as equipment which provides the high-shear stress necessary for the intimate mixing of oxygen with medium-consistency pulp. It shall include mechanical mixers of the "high-shear" type, medium-consistency centrifugal pumps which create a turbulent, high-shear zone at their discharge suitable for mixing, refiners, and "static" or "motionless" mixers in the case where they impart high-shear stress on pulp suitable for oxygen mixing.

A retention tube is also added between the Chlorine and Extraction stages at a point after alkali and steam addition and the added dynamic mixer. A thick stock or medium consistency pump is also required if not already present in-line. Oxygen is added using the dynamic mixer to effect good mass transfer of the oxygen into the alkylime pulp. Conventional wisdom holds that oxygen mass transfer is the limiting factor; i.e., to get acceptable process results, the oxygen must be rapidly and intimately contacted with the alkaline pulp. The function of the "retention tube" is that of an oxygen reactor; i.e., to allow sufficient time and pressure for the oxygen to react/bleach the pulp before entering the E-tower. A minimum reaction/retention time of 2-2 minutes under pressure is required. If the E-stage operates in the pulp upflow mode, or a displacement bleach tower is used, a retention tube is not required.

In summary, to achieve the benefits of E_0 , a significant investment is required in additional operating equipment as well as continuing significant power costs to operate the dynamic mixer. These costs have deterred more rapid acceptance of this technology and certainly reduced its financial attractiveness.

PRIOR ART

The following disclosures are representative of prior art practices in pulp treatment, employing an alkali extraction step in the multi-stage bleaching sequence.

U.S. Patent 4,451,332 is concerned with multi-stage bleaching of ligno-cellulose containing fiber material in which oxygen-containing gas is employed in an alkali extraction step. The oxygen-containing gas is mixed with the cellulose fiber material in a manner so as to form a foam of these, which foam, without an intervening oxidation step, is subjected to alkali extraction in upward flow. The method is aimed at production of a bleached delignified fiber product without bleaching the extracted lignin, and to suppress the problem of lignin condensation causing pulp discoloration. The oxidative extraction can be employed as a step in various multi-stage sequences of the prior art.

Early mill trials employing oxygen reinforced alkali extraction as a step in the multi-stage bleaching sequence are described in Proceedings of the Technical Association of the Pulp and Paper Industry (TAPPI) 1981 Annual Meeting at pages 279 to 284. A dynamic oxygen mixer was installed ahead of the first alkali extraction tower of an existing plant, operating to thoroughly disperse the oxygen into the pulp

suspension. It was found that not only were significant cost savings obtained by the oxygen reinforced alkali extraction but better pulp washing was experienced.

Actual U.S. plant start up and operating experiences employing oxygen alkali extraction (E_0) in the pulp bleaching sequence are described in TAPPI Proceedings, 1983 Pulping Conference, at pages 309-313 and 315 to 322. In these operations a dynamic mixer was also employed to obtain good mixing of the oxygen gas with the pulp suspension.

Prior art practice is to intimately mix oxygen with pulp by a dynamic mixer quickly after addition of alkali. Mixing is generally important in any three phase system, such as oxygen/water/pulp, where mass transfer can be the rate-limiting step. Not surprisingly, then, in all known successful commercial E_0 processes, a dynamic mixer has been employed. Others have unsuccessfully attempted to practice the technology in the absence of dynamic mixers by direct addition of oxygen into the extraction tower. The rationale offered for these failures has been poor mass transfer of oxygen to the bleach liquor. Conventional thinking has been that this reduced mass transfer rate does not permit complete reaction of oxygen to occur within the limits of available retention time. Our observation is that other phenomena are involved; specifically, the delay of oxygen arrival at the reaction site permits undesirable reactions to occur between the chlorinated pulp and alkali which create lignin products less reactive toward oxygen.

The present invention, among other benefits, provides a process which achieves the desirable benefits of oxygen alkali extraction (E_0) without being committed to the requirement for oxygen addition quickly after alkali addition or to the costly investment of a dynamic mixer.

SUMMARY OF THE INVENTION

In accordance with the present invention the beneficial advantages of oxygen alkali extraction are obtained in the absence of a dynamic mixer and/or without the requirement for oxygen addition quickly after alkali addition. This unexpected result is achieved by mixing alkaline pulp with molecular oxygen and a small amount of a co-oxidant, at a point either before or within an alkaline bleaching stage of a ligno-cellulose pulp delignification and bleaching process carried out in order to increase pulp brightness and/or to reduce chlorine-based chemical consumption of subsequent bleaching stages.

The operation of the invention will be fully understood and its several advantages appreciated from the detailed description which follows read in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic flow diagram of a conventional prior art multi-stage bleaching system employing a down-flow E-stage preceded by an upflow retention tube, modified in accordance with an embodiment of the present invention to provide for oxygen/co-oxidant introduction.

Figure 2 is a schematic flow diagram of a conventional prior art multi-stage bleaching system employing a down-flow E-stage without retention tube, modified in accordance with an embodiment of the present invention to provide for oxygen/co-oxidant introduction.

Figure 3 is a schematic flow diagram of a conventional prior art multi-stage bleaching system employing an upflow E-stage, modified in accordance with the present invention to provide for oxygen/co-oxidant introduction.

Figure 4 is a schematic flow diagram of a conventional prior art displacement bleaching system modified in accordance with the present invention to provide for oxygen/co-oxidant introduction.

Figure 5 is a schematic flow diagram of a prior art multi-stage bleaching system having a hypochlorite stage, modified in accordance with the present invention to provide for oxygen introduction in the hypochlorite stage.

Figures 6 to 9 are graphic plots of data reported in the included tables comparing obtained pulp brightness at progressive levels of ClO_2 used, in various modifications in operation of the bleach sequences.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

Implementation of the invention can take various forms as is illustrated by the several examples set out
 5 below.

Figure 1 illustrates application of the invention in a typical prior art multi-stage pulp bleaching system having a retention tube just prior to the alkaline extraction stage (E). As seen in Figure 1, the unbleached pulp enters the bottom of tower 10 in which it is treated with chlorine (C) and discharges from the top of tower 10 into a washing section 12 wherein the chlorinated pulp is washed with water in conventional
 10 manner. The washed pulp is discharged from 12 via line 14 into which line sodium hydroxide is added. The resulting thick stock is then introduced by means of a thick stock pump or medium-consistency pump 15 into the bottom of a retention tube 16, the pulp being contacted with molecular oxygen in the line after the thick stock or medium consistency pump, at the bottom of the retention tube, or within tower 18. The pulp stock flows upwardly through tube 16, discharging into the top of downflow tower 18. In the known prior art
 15 systems employing "Oxygen Alkali Extraction" (E₀) the molecular oxygen is generally contacted with the stock discharged from the pump 15 by adding the oxygen to a new dynamic mixer to effect efficient high-shear mixing before admission into the retention tube 16. In prior art systems of the type shown modified according to the present invention in Figure 1, having a retention tube preceding the downflow E-stage, the dynamic mixer was located prior to the inlet of the retention tube for addition of oxygen quickly after alkali
 20 addition. In the modified system of the present invention there is no need for near simultaneous O₂/alkali addition nor for a dynamic mixer, hence, as illustrated in the Figure 1 embodiment, the thick stock leaving pump 15 flows directly into the bottom of retention tube 16 and discharges from the top of that tube directly into extraction tower 18. Molecular oxygen is introduced either immediately after pump 15, into the bottom tube 16 or directly into tower 18. The co-oxidant employed in accordance with the invention may be
 25 introduced into the stock upstream of pump 15, into the stock discharged from pump 15, into the bottom of tube 16, or directly into the top of tower 18. The alkaline pulp having been treated with molecular oxygen and co-oxidant is withdrawn from the bottom of tower 18 by a pump 19 and washed at 20. The washed pulp is discharged from 20 via line 22 and pumped into the bottom of tower 25 by pump 24. In tower 25 the pulp is treated with ClO₂ (D) introduced into the line entering tower 25.

30 The pulp flows upwardly through treating tower 25 and discharges at the top of the tower into a wash station 26. The washed pulp leaves 26 via discharge line 28 and is pumped by means 29 into the top of a second downflow extraction tower 30. Additional NaOH is added into the pulp at line 28.

From the bottom of tower 30 the treated pulp is pumped by means 35 to a wash station 36. The washed pulp discharged from 36 via line 37 is pumped at 38 into a second upflow tower 39. Additional ClO₂ is introduced into the pulped stream entering the bottom of tower 39. Leaving the top of tower 39 the pulp is again washed at 40 and discharged via line 41 as bleached pulp.

The system illustrated in Figure 1 operates in the bleaching sequence C E₀ D E D. The introduction of molecular oxygen and co-oxidant in the E-stage can similarly be practiced in plants having a bleach sequence other than that illustrated in Figure 1, as for example, in systems in which the C Stage is
 40 substituted by a C_D or D/C stage with or without a preceding O stage, as well as in systems having a lesser number of stages, e.g. C E₀ D, CE₀HD.

In the system illustrated in Figure 2, there is no retention tube preceding the downflow E-stage tower, but there is an upflow pipe 17. As illustrated the unbleached pulp is initially introduced into tower 10 in which it undergoes treatment with chlorine. The other treating towers and auxiliary equipment are the same
 45 as those of Figure 1 and are similarly numbered. As seen in Figure 2, molecular oxygen may be admitted into the pulp stock at the discharge outlet of pump 15 and/or into upflow pipe 17 and/or directly into tower 18. The co-oxidant may be introduced at one or more points between the discharge of washing unit 12 and at or near the top of tower 18. In other words, in the embodiments of Figures 1 and 2 as well as in other arrangements employing molecular oxygen/co-oxidant in the E₀-stage the oxygen can be added nearly
 50 simultaneously with the co-oxidant or after the co-oxidant but preferably not before the co-oxidant. In embodiments, such as those illustrated in Figures 1 and 2, employing at 15 a medium consistency centrifugal pump, it is not necessary to add the gaseous oxygen into the high-shear zone at the pump discharge as taught by prior art, but, rather, the oxygen can be applied directly into the pulp at a location convenient to the plant-specific configuration.

55 In the Figure 3 embodiment, the illustrated system is one employing an upflow E-stage, but otherwise operating in the same sequence as that illustrated in Figure 2, CE₀DED. Similar parts of the illustrated apparatus have the same numbering as in Figures 1 and 2. The thick stock discharged by pump 15 is discharged into the bottom of upflow tower 18. Oxygen is introduced directly at or near the bottom of tower

18; the co-oxidant may be introduced at the same level as the oxygen or upstream of that level in tower 18 or into the line entering the bottom of that tower.

Figure 4 illustrates a typical prior art system for practice of displacement bleaching modified in accordance with the invention for introduction of oxygen gas and co-oxidant. Unbleached pulp is pumped by means of 40 and mixed in a known manner at 41 with chlorine, chlorine dioxide and water. The pulp is discharged into the bottom of multilevel displacement bleach tower 45. In tower 45 the pulp flows upward through a series of zones where treatment with bleaching chemicals occurs. Each zone replaces an individual stage or tower in a conventional bleach plant. There is no difference between the chemistry of displacement bleaching and that of convention bleaching. However, in a displacement bleach tower bleaching chemicals are displaced through the pulp mat rather than mixed into the pulp in a conventional manner. The equipment required to effect this displacement is wholly contained within tower 45. Bleaching chemicals are transported to the appropriate zones via central shaft 42. Extraction zone 43 replaces the first extraction stage of conventional bleach plant.

In zone 43 the pulp can be treated with oxygen and co-oxidant in a manner chemically identical to that described previously for a conventional bleach plant. Methods of introducing oxygen and a co-oxidant into the extraction zone are depicted in figure 4. Oxygen and co-oxidant can be dispersed into the sodium hydroxide (extraction) solution at location 44 which passes down through shaft 42 and is diffused radially into zone 43 or added into the extraction zone through the side of the tower.

Figure 4 depicts only one bleaching sequence that can be performed by displacement bleaching. The invention for introduction of oxygen gas and co-oxidant can be applied to a displacement bleach plant regardless of the bleaching sequence if an alkaline zone is present.

Figure 5 is a schematic flow diagram for introduction of oxygen into a conventional multi-stage pulp bleaching system employing an existing alkaline hypochlorite treating tower (H). The unbleached pulp is introduced into the bottom of tower 50 in which it is treated with chlorine introduced into feed line 51. The chlorinated pulp discharged at the top of tower 50 is washed at 52 and the washed pulp leaving the washer via line 54 is pumped at 55 into the top of tower 58. Sodium hydroxide is introduced into line 54 downstream of washer 52. Initial alkaline extraction (E) takes place as the pulp descends in tower 58. The pulp discharged from the bottom of tower 58 is again washed at 60 and the washed pulp discharged via line 62 is passed to the top of the hypochlorite treating tower 64, the hypochlorite treating solution being introduced into line 62.

In a system such as that illustrated in Figure 5, employing CEHD sequence, the oxygen can be added as described for the CE₀DED sequence (Fig. 3) or without additional co-oxidant. The oxygen can be added prior to the H-stage (after hypochlorite application) or directly to the H-stage. Thus, as depicted in the Figure 5 embodiment of the invention, oxygen is introduced prior to or directly into tower 64 in which the pulp is undergoing treatment with alkaline hypochlorite.

After treatment in tower 64 the pulp is washed at 66 and passed via line 68 and pump 70 into tower 72 in which it is subjected to treatment with ClO₂, washed at 74 and discharged as bleached pulp.

In each of the several described embodiments, as indicated above, the oxygen can be added nearly simultaneously with the co-oxidant or after the co-oxidant. The oxygen may be added at any designed dosage; generally six to eleven pounds of oxygen per ton of oven-dry pulp is satisfactory. The oxygen may be introduced in any convenient manner such as by one or more diffusers after pump 15, or it may be sparged directly into existing equipment. The co-oxidant may be alkali or alkaline earth hypochlorite, chlorine, or hydrogen peroxide. Alkali hypochlorite is preferred due to its relative cost effectiveness. The choice between hypochlorite and peroxide can be based on existing on-site availability and economics. The co-oxidant may be added in dosages up to 5 weight percent on pulp, but preferably in the range of 0.2-2.0% (oven-dry basis) with pulp of medium consistency. Instead of purchased co-oxidant one may employ that piped in from another part of the bleach plant, if available.

In the experimental runs set out below commercial unbleached kraft pulp (brownstock), consisting of pine wood species blended with less than 10 weight % hardwood species, was used in the reported examples. The initial Kappa number of the pulp as 28.7, and exhibited a 0.5% CED viscosity of 30.1 mPa. The data obtained from several basic types of bleaching sequences were noted and the results of the different sequences listed below were compared.

C_DEDED Which is representative of a conventional 5-stage sequence (no oxygen).

C_DED Which represents results achievable with only 3 stages of conventional bleaching (no oxygen).

C_DE₀D Which represents results achievable with conventional E₀ (oxidative extraction) wherein a dynamic mixer is employed to rapidly and efficiently/intimately mix oxygen with the chlorinated pulp quickly after alkali addition and prior to introduction of the pulp into the E-stage.

C_DE₀H_D Which represents results achievable with conventional E₀ (above) in the presence of

hypochlorite.

$C_D E \overset{!}{O} D$ Which is similar to the above except the pulp is not contacted by O_2 quickly after or simultaneous with alkali addition as with conventional E_O . Instead, O_2 addition is delayed. This simulates the reduced (adverse) E_O effect that occurs as a consequence of exposing chlorinated pulp to alkali in the absence of oxygen or poor O_2 /pulp mixing such as occurs with direct injection of oxygen not before, but into the E-stage; or before the E-stage without use of a dynamic mixer to allow rapid mixing and reaction of the chlorinated pulp with the oxygen.

$C_D E \overset{!}{O/H} D$ Which represents the improved results achievable with $C_D E \overset{!}{O} D$ in the presence of hypochlorite.

$C_D E \overset{!}{O/P} D$ Which represents the improved results achievable with $C_D E \overset{!}{O} D$ in the presence of hydrogen peroxide without use of a dynamic mixer.

Using typical bleach plant operating conditions (chemicals, temperatures, time, etc.), the usual laboratory procedures were followed in simulating the bleach plant process.

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a. Chlorination (C_D) Stage:

Crumbed pulp was placed in a polyester bag and an amount of chlorine water and chlorine dioxide added to make the charge 5.45% and 0.365% respectively. 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 Alkali Extraction (E) Stage:

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Chlorinated pulp was placed in a Hobart lab mixer with water followed by sufficient caustic (sodium hydroxide) solution to bring the pulp consistency to 10% and the alkali charge to 3.21%. After two minutes of agitation, the contents were transferred to a polyester bag, which was sealed and placed in a constant temperature bath at 70 °C for 60 minutes. Upon completion of the extraction, the pulp was filtered (effluent pH = 11.5) and the pulp washed with water.

c. Conventional Oxygen Alkali Extraction (E_O) Stage:

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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 provided by a dynamic mixer. The reactor was preheated while the alkali and pulp were mixed as described above for conventional extraction (E). 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. Oxygen was immediately added to the reactor to 25 psig and the temperature raised immediately (<1 min) to 70 °C. After 4-10 minutes exposure to oxygen, the oxygen was vented, and the extraction was allowed to proceed an additional 35-45 minutes without oxygen in order to simulate the extraction stage. The separate pulp samples were then removed, washed with water, and prepared for the dioxide bleaching stage.

d. Unconventional Oxygen Alkali Extraction ($E \overset{!}{O}$):

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This procedure, involving delayed oxygen addition, is to simulate the adverse impact of not using a dynamic mixer and/or not contacting the alkaline chlorinated pulp with oxygen quickly after alkali addition. The same reactor, conditions, and procedure was utilized as described above for conventional oxygen alkali extraction except admission of oxygen was delayed for 15 minutes after the pulp had been brought to 70 °C, i.e., 15 minutes after caustic was added. The oxygen contact time remained 4-10 minutes as before, at which point the reactor was vented and the extraction allowed to proceed at 70 °C for a total period of 45 minutes.

e. Hypochlorite (or Peroxide) Promoted Oxygen Alkali Extraction (E_{H_2O} , E_{H_2O} , $E_{P/O}$):

The respective procedures above were followed except in the initial step, chlorinated pulp, alkali, and hypochlorite or peroxide were simultaneously mixed in a Hobart mixer prior to conducting the respective oxidative extraction reaction, i.e., alkali and co-oxidant were added prior to the oxygen. The hypochlorite and peroxide charge was 0.5% and 0.7%, respectively, on pulp.

f. Chlorine Dioxide (D) Stages:

Each individual pulp sample, removed from the trays of the extraction reactor, were 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 (0.1 to 2.2% on pulp) followed by sufficient water to bring pulp consistency to 12%. The bag was sealed and rapidly brought to 70 °C and maintained at this temperature for 3 hours. At this time, an aliquot of bleach liquor was removed and analyzed for residual dioxide. If the dioxide treatment was the last stage of the particular bleach sequence, the pulp was treated with sulfur dioxide to bring the pH to 3.

g. Other Procedures:

Kappa number, viscosity, handsheets, and GE brightness determinations were made in accordance with the respective TAPPI Standard Test Procedures. Chemical charges are on a weight percent basis; pulp weight is air dry basis.

• Example 1 (C_D ED and C_D EDED):

The purpose of this laboratory simulation is to provide comparative base case data on the effectiveness of experimental conventional bleaching on the brownstock. Following the general procedures outlined above, brownstock was subjected first to a C_D ED sequence, and then a portion of each dioxide (D_1) sample was further treated to yield C_D EDED data. In the last dioxide (D) stage of each sequence, brightness vs. required dioxide charge profiles were developed to measure the required dioxide consumption to achieve a given brightness level and to show what maximum level of brightness could be achieved. The results obtained are set out in Table 1 below:

TABLE 1

E ₁ Stage	D ₁ Stage		D ₂ Stage	
	K# = 5.47	% ClO ₂	Brightness	% ClO ₂
	0.8	68.4	0.2	85.1
			0.4	87.8
			0.6	88.6
			0.2	88.9
			0.4	89.9
			0.6	90.5
	1.0	78.3	0.2	88.3
			0.4	90.0
			0.6	90.5
	1.2	77.0	0.2	90.1
			0.4	91.0
			0.6	90.9
1.5	80.2	0.2	90.1	
		0.4	91.0	
		0.6	90.9	

• Examples 2A and 2B (C_DE_OD):

The purpose of this example is to provide comparative base case data on the effectiveness of a conventional bleaching sequence that incorporates a conventional oxygen alkali extraction (E_O) stage with a dynamic mixer; i.e., oxygen is added quickly after the alkali under conditions of intimate contact with the pulp.

Following the general procedure outlined above, brownstock was subjected to a C_DE_OD bleach sequence. The experiment was identical to that described in Example 1 for the C_DED sequence except for the oxygen stage which was carried out as described in the general procedure in a manner to simulate conventional E_O. In a bleach plant, alkali is added to washed chlorinated pulp and heated to about 70 ° C with steam. The hot pulp is then rapidly pumped to a point at which oxygen is immediately contacted intimately with the pulp using a dynamic mixer, which effects good mass transfer of the oxygen into the pulp slurry. The oxygen/pulp slurry then passes through a length of process pipe ("retention tube") sized to give the oxygen at least 2-4 minutes reaction time under pressure with the pulp prior to introduction to the alkaline E-stage/tower. In effect, the O₂/alkali are nearly simultaneously added in the pulp, and the pulp's reaction with oxygen complete before it enters the E-tower.

In the laboratory simulator washed chlorinated pulp from the C_D-stage was charged with alkali and dispersed in a thin layer over several trays in the oxygenation reactor to maximize intimate contact of the O₂/pulp. The reactor vessel was heated to 70 ° and brought to 25 psig with oxygen. After either a 4 or 10-minute oxygen contact time, the oxygen was removed and the caustic reaction was allowed to proceed an additional 40 or 35 minutes, respectively, to simulate conditions within the extraction (E) tower.

The results obtained for this C_DE_OD sequence are set out in Table 2 below and are compared in Figure 6 with the C_DED results from Example 1.

Table 2

E ₁ Stage	D ₁ Stage	
K# = 3.96 (4.14)	% ClO ₂	Brightness
	0.5 (0.5)	74.8 (76.0)
	0.8 (0.8)	82.4 (84.1)
	1.0 (1.0)	84.8 (85.2)
	1.2 (1.2)	86.7 (86.3)
NOTE: Values before parentheses are with a 10 minute oxygen contact time (example 2A). Values in parentheses are with a 4 minute oxygen contact time (example 2B).		

The data clearly show not only the already known positive effect of oxygen in a conventional E_O bleach sequence in reducing the requirement for chlorine dioxide to achieve target pulp brightness levels, but also that comparable results are obtained with either a 4 or 10-minute oxygen contact time.

• Examples 3A and 3B (C_DE_O D):

The purpose of this example is to demonstrate that when quick and efficient oxygen contact with the pulp following alkali addition (such as with the dynamic mixer of conventional E_O wherein O₂ is added quickly after alkali and prior to the first E-stage) is absent, secondary chemical phenomena occur precluding attainment of the maximum E_O benefits.

To demonstrate this negative effect, the experiment described in Example 2 was repeated except the

addition/mixing of oxygen was delayed 15 minutes. (4 minute and 10 minute oxygen contact times were used). The results obtained are reported in Table 3 below and are summarized in Figure 6 (curve III) along with the results obtained from Examples 1 and 2. In Figure 6 curve I and II are plots of the data of Tables 1 and 2 respectively.

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Table 3

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E ₁ Stage	D ₁ Stage	
K# = 4.38 (4.55)	% ClO ₂	Brightness
	0.8 (0.8)	76.8 (76.6)
	1.0 (1.0)	82.4 (81.9)
	1.2 (1.2)	84.4 (84.5)
	1.4 (1.4)	85.5 (85.4)
NOTE: Values before parentheses are with a 10-minute oxygen contact time (example 3A). Values in parentheses are with a 4-minute oxygen contact time (example 3B).		

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These results, when compared to those obtained in Example 2, clearly show:

(a) When O₂ addition is delayed (not added quickly after the alkali) significantly inferior results are obtained even with an extended oxygen contact time of 10 minutes.

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(b) The absence of a dynamic mixer to facilitate the rapid interaction of O₂ with the alkaline pulp will lead to inferior process results, even when the oxygen contact time (10 minutes) is more than double that of conventional E₀.

(c) Direct in-line (no high shear mixing) addition of oxygen to the pulp stream after alkali addition up to and including direct injection of oxygen into the E-stage/tower will lead to inferior results; even when mass transfer of oxygen to the pulp slurry is optimal.

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• Example 4 (C_DE₀/HD):

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The purpose of this example is to demonstrate that the presence of low levels of hypochlorite will reverse the negative effect demonstrate in Example 3, overcome the requirement for quick and efficient mixing of alkali/pulp/ O₂, and allow the successful practice of direct, in-line oxygen injection technologies in the absence of dynamic mixers at any point after alkali addition including directly into the pulp transfer lines or directly into the E-tower.

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The experiment described in Example 3A was repeated except a 0.5% charge of hypochlorite was added along with the alkali. As before, the system was brought to temperature and after a 15-minute delay, the pulp was then contacted with oxygen for 10 minutes followed by the usual alkali extraction. The results obtained are set out in Table 4 below and are compared in Plot IV of Figure 7 with the results of Example 2 and 3 (curves II and III).

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Table 4

E ₁ Stage	D ₁ Stage	
	K# = 4.11	Brightness
	0.8	80.7
	1.0	84.0
	1.2	85.4
	1.4	85.9

The results clearly show that in the presence of hypochlorite, essentially equivalent oxygen alkali extraction results can be obtained without regard to when or where the oxygen is added and without employing dynamic mixers.

• Example 5 (C_DE₁O₁/P/D):

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The purpose of this experiment is to demonstrate that the process is not limited to hypochlorite based chemicals, but that other co-oxidants like hydrogen peroxide are also effective.

The experiment described in Example 4 was repeated except instead of sodium hypochlorite, a charge of 0.7% hydrogen peroxide was added. A 2% charge of sodium silicate was also added to stabilize the peroxide. The oxygen contact time was 4 minutes. The results obtained are set out in Table 5 below and plotted in Figure 8 (curve V).

Table 5

E ₁ Stage	D ₁ Stage	
	K# = 3.50	Brightness
	0.5	77.8
	0.8	81.9
	1.0	85.9
	1.2	86.7
	1.4	87.6

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The results clearly show that peroxide is also an effective enabling agent for direct oxygen injection.

45 • Example 6 (C_DE₀/H/D):

The purpose of this example is to demonstrate that the effectiveness of this process is not due simply to adding an additional oxidant to the bleach process.

The experiment described in Example 2, which simulates conventional oxygen alkali extraction (E₀) with a dynamic mixer, was repeated in the presence of a 0.5% and 1.4% charge of hypochlorite. The results obtained are set out in Table 6 below and are plotted in Figure 9 along with those obtained in Example 2.

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Table 6

5	<u>E₁ Stage</u>	<u>D₁ Stage</u>	
	<u>K# = 4.03</u> (3.85)	<u>% ClO₂</u>	<u>Brightness</u>
		0.8 (0.8)	83.8 (82.6)
		1.0	85.2
10		1.2 (1.2)	86.2 (86.8)
		1.4	86.7

NOTE: The values in parentheses are at the 1.4% hypo charge.

The results clearly show that within experimental error, the presence of hypochlorite does not materially improve the conventional oxygen alkali process.

• Example 7 (C_DEHD):

In a commercial scale test in a C_DEHD bleach plant operating at 12 tons per day bleached softwood pulp, a total of 2500 SCFH oxygen was injected through spargers located in each of 4 ports of the dilution zone ring at the base of the downflow H-tower (see Figure 5). The test was conducted over a period of several days, alternately interrupting the oxygen flow to ascertain results in the absence of oxygen. The average values observed were 51.2 lbs. hypo consumed per ton pulp without oxygen, and 45.2 lbs. hypo consumed per ton pulp in the presence of oxygen.

Claims

1. In the sequential delignification and bleaching of lignocellulosic pulp where the pulp is subjected to treatment in sequence with various delignification and bleaching chemicals and wherein during such sequence it is subjected to at least one stage of alkali extraction, the method which comprises alkalinizing the pulp during a stage in said sequence, introducing oxygen-containing gas directly into the alkaline pulp without the use of a dynamic mixer, and treating the alkaline pulp with the oxygen-containing gas in the presence of added co-oxidant selected from the group consisting of alkali metal and alkaline earth metal hypochlorites, chlorine and hydrogen peroxide.

2. The method as defined in Claim 1 wherein at least the first of said alkali extraction stages is carried out in a downflow reactor preceded by an upflow retention interval, and said co-oxidant is added at the start of said retention interval or introduced into said downflow reactor.

3. The method as defined in Claim 1 wherein at least the first of said alkali extraction stages is carried out in downward flow, the alkalinizing being effected after the pulp has undergone a C, D/C or C_D stage, and the oxygen-containing gas being introduced subsequent to the addition of co-oxidant to the pulp.

4. The method as defined in Claim 1 wherein the first of the E stages is performed in upward flow, said oxygen-containing gas and co-oxidant being added to the pulp prior to or during said first E stage.

5. The method as defined in Claim 1 wherein said bleaching sequence includes a hypochlorite treatment of the pulp following alkali extraction, said hypochlorite treatment being carried out in the presence of oxygen-containing gas added to the pulp.

6. The method as defined in Claim 1 wherein the oxygen-containing gas is introduced in an amount to provide 6 to 11 lbs. of oxygen per ton of oven dry pulp.

7. The method as defined in Claim 6 wherein said co-oxidant is added in dosage of up to 5 weight per cent of pulp on oven-dry pulp basis.

8. The method as defined in Claim 6 wherein said co-oxidant is added to pulp of medium consistency at a dosage of 0.2-2% by weight of pulp on oven-dry basis.

9. The method as defined in Claim 1 wherein said co-oxidant is added to the pulp in a dosage of up to 5% by weight by pulp on oven-dry pulp basis.

10. The method as defined in Claim 1 wherein said alkali extraction stage directly follows a chlorination stage with molecular chlorine in the presence or absence of ClO_2 .

5 11. In the sequential bleaching of lignocellulosic pulp wherein the pulp is subjected to treatment in sequence with various bleaching chemicals and during such sequence it is subjected to at least one stage of treatment with an alkali metal hypochlorite or an alkaline earth metal hypochlorite following an alkali extraction step, the improvement which comprises effecting such hypochlorite treatment in the presence of gaseous oxygen introduced into the alkali-extracted pulp prior to or during the stage when the pulp is
10 undergoing treatment with the hypochlorite.

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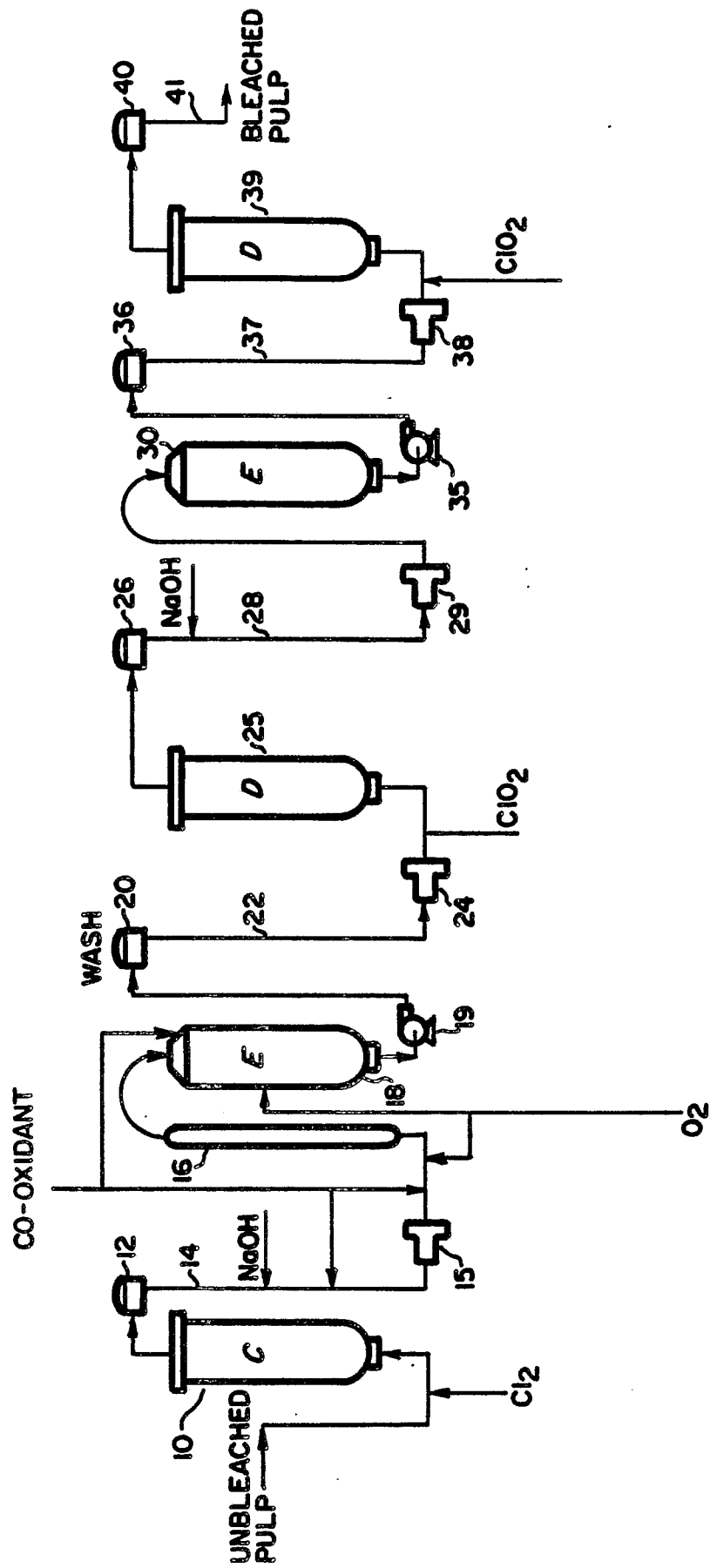


FIG. 1

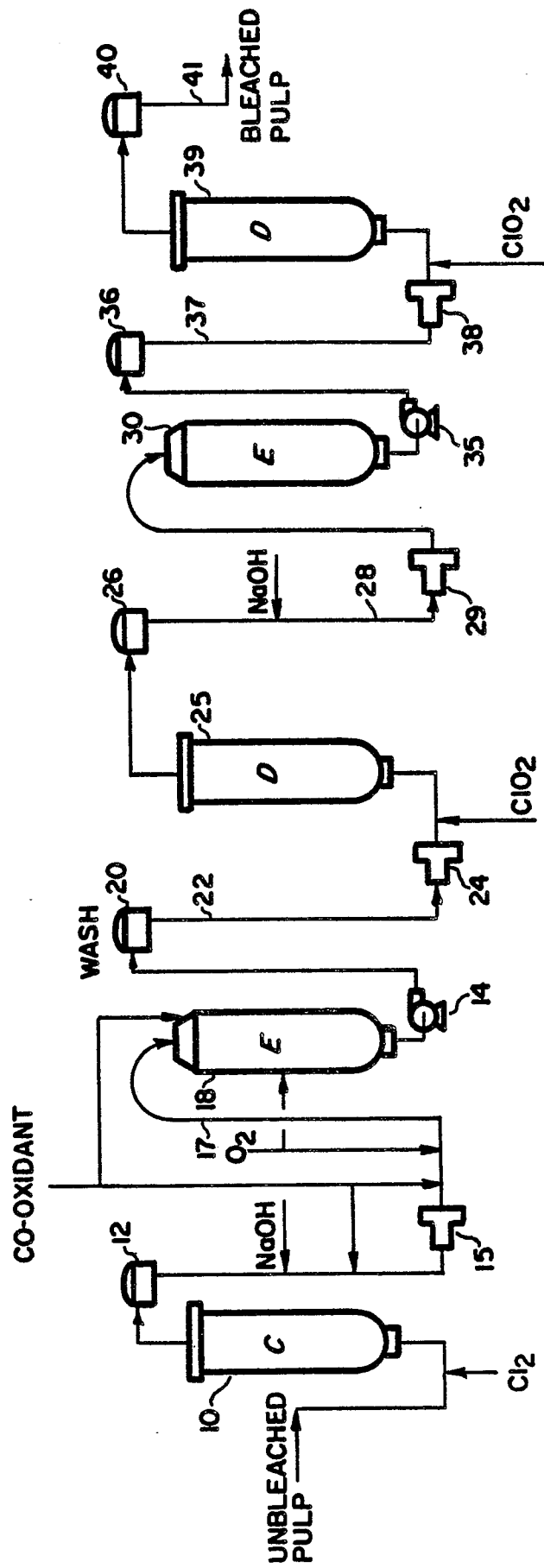


FIG. 2

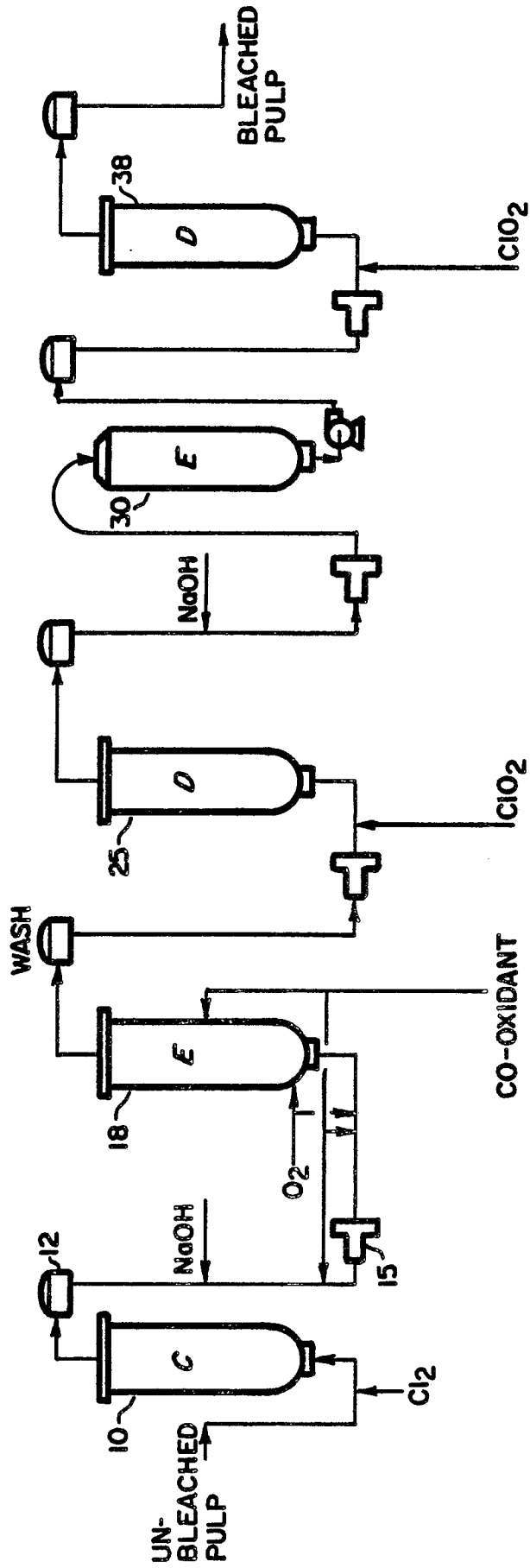


FIG. 3

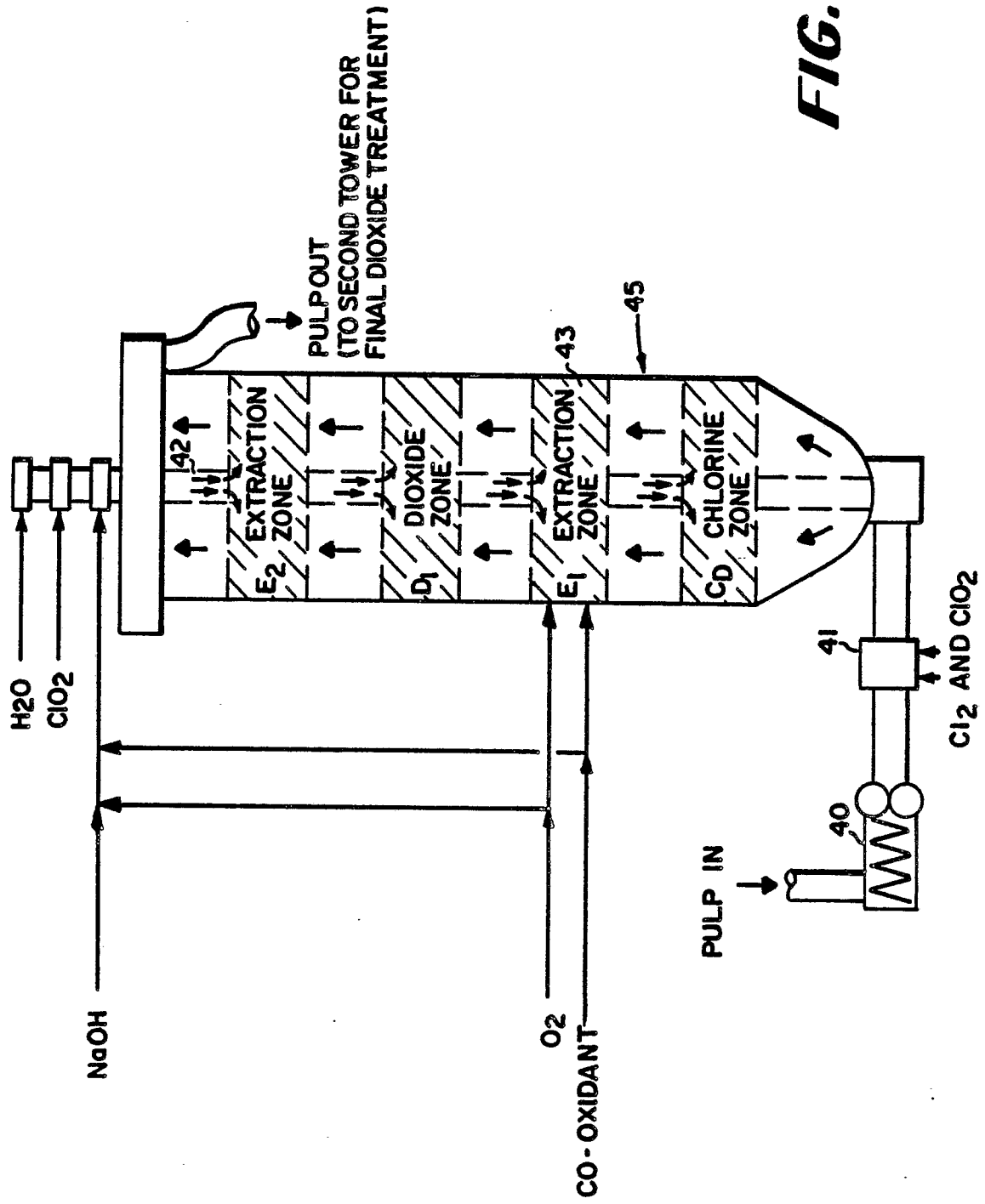


FIG. 4

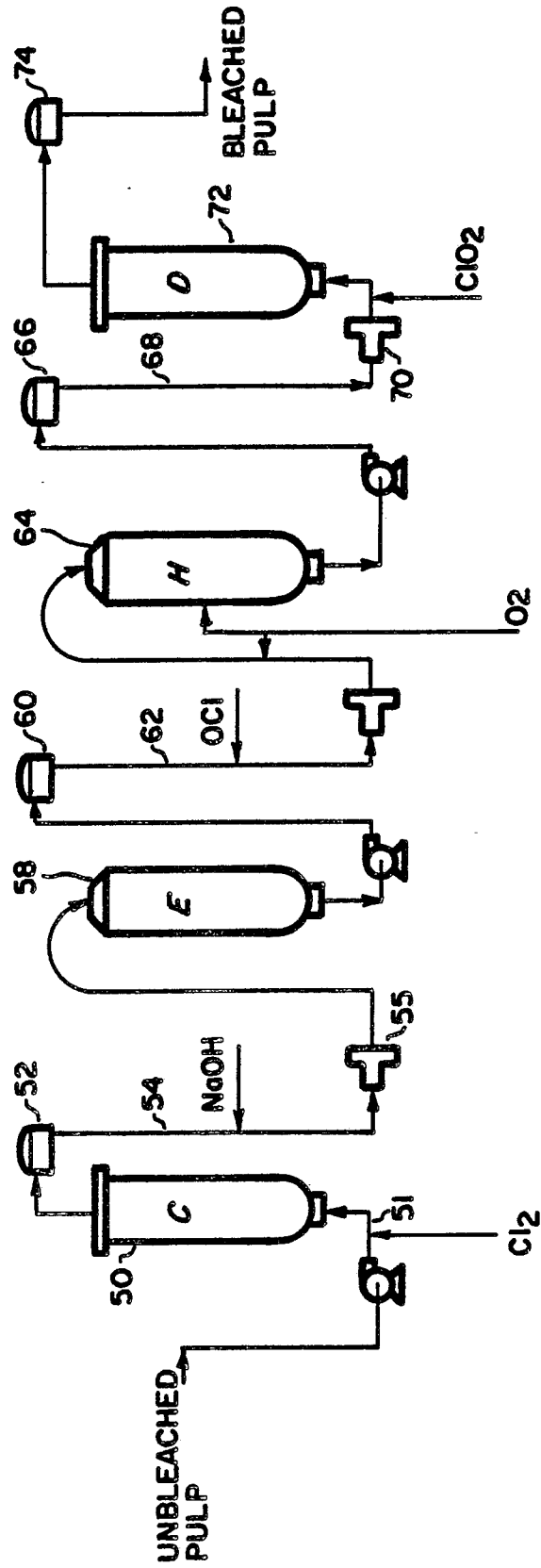


FIG. 5

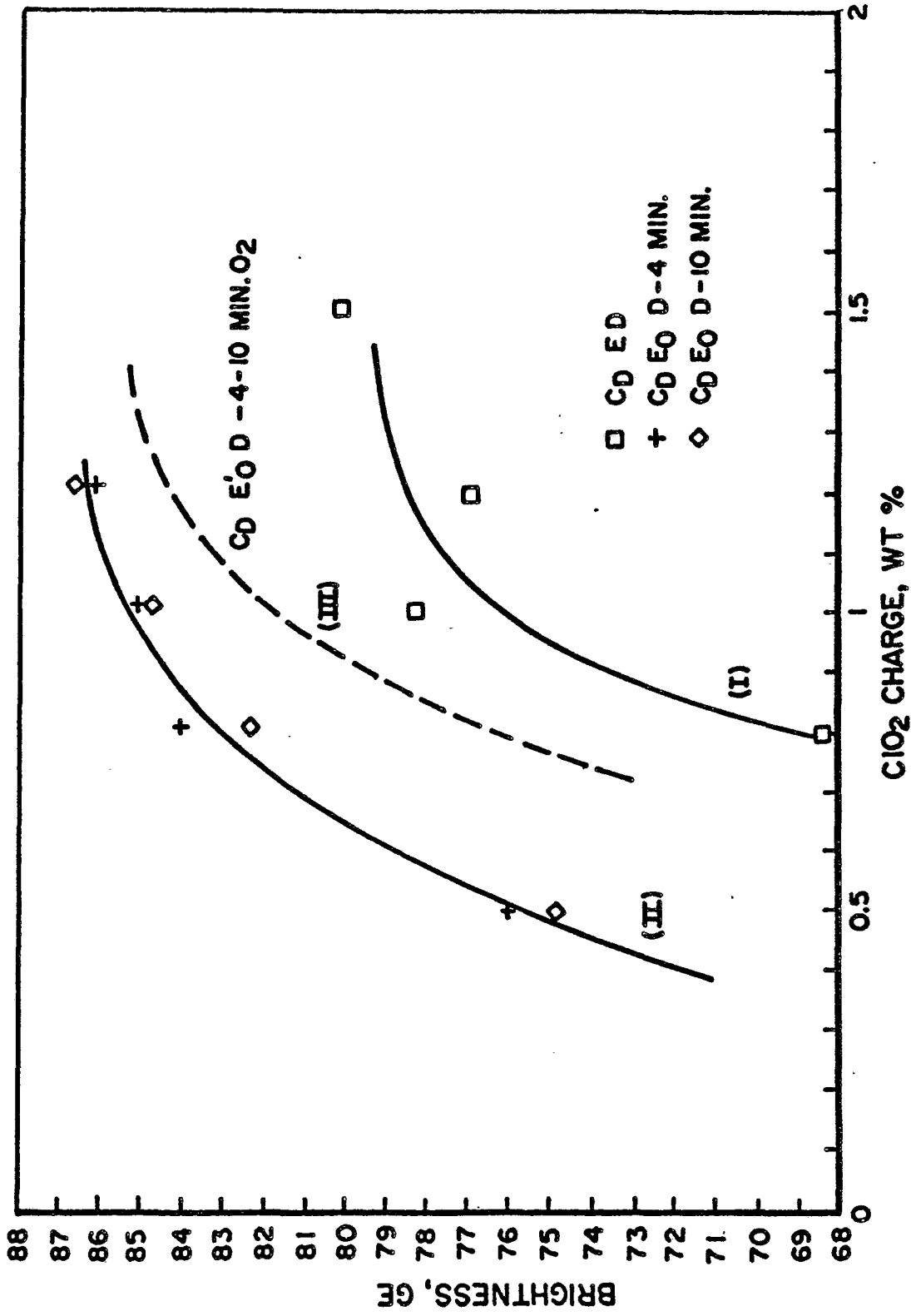
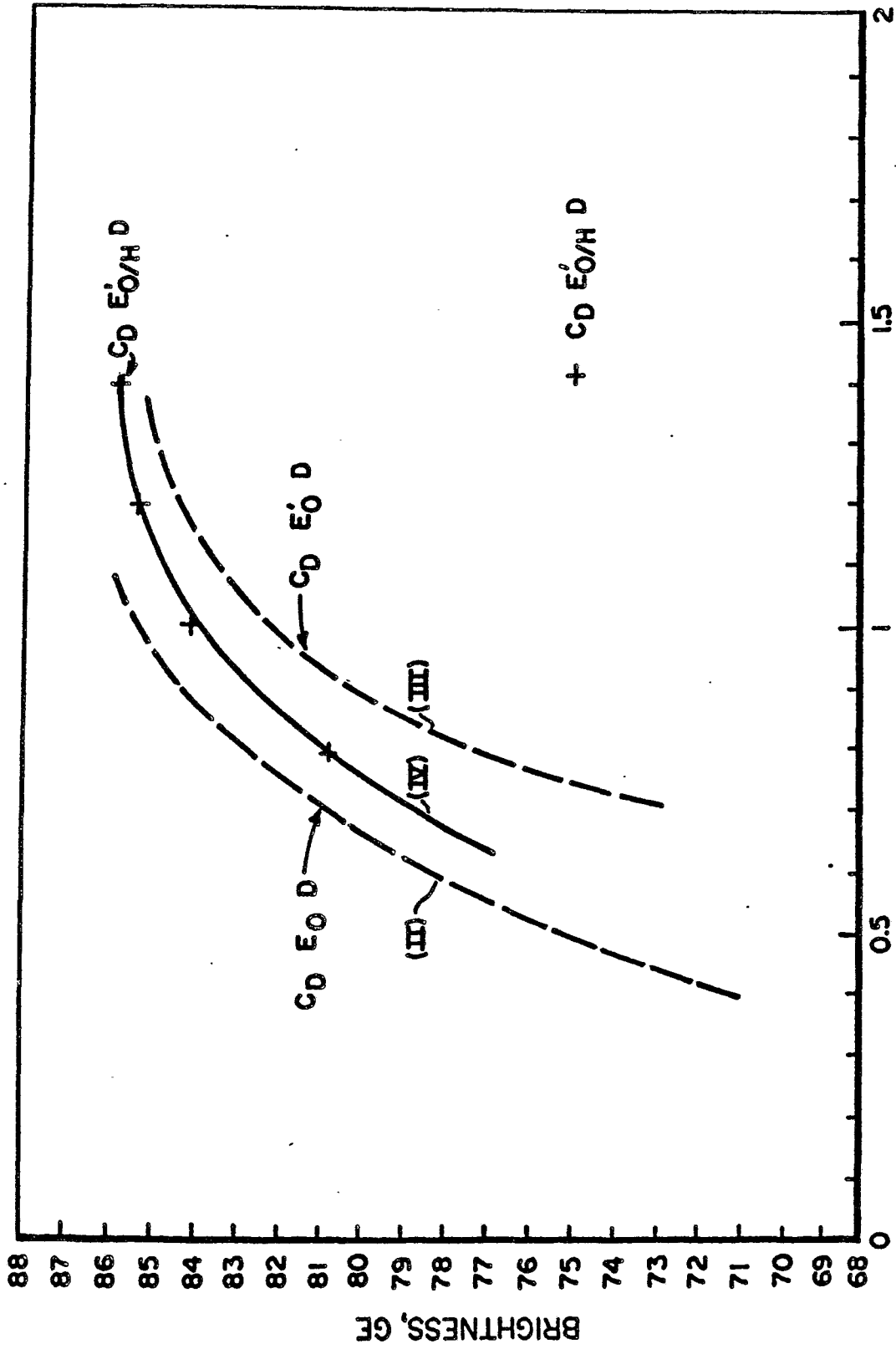


FIG. 6



ClO2 CHARGE, WT %

FIG. 7

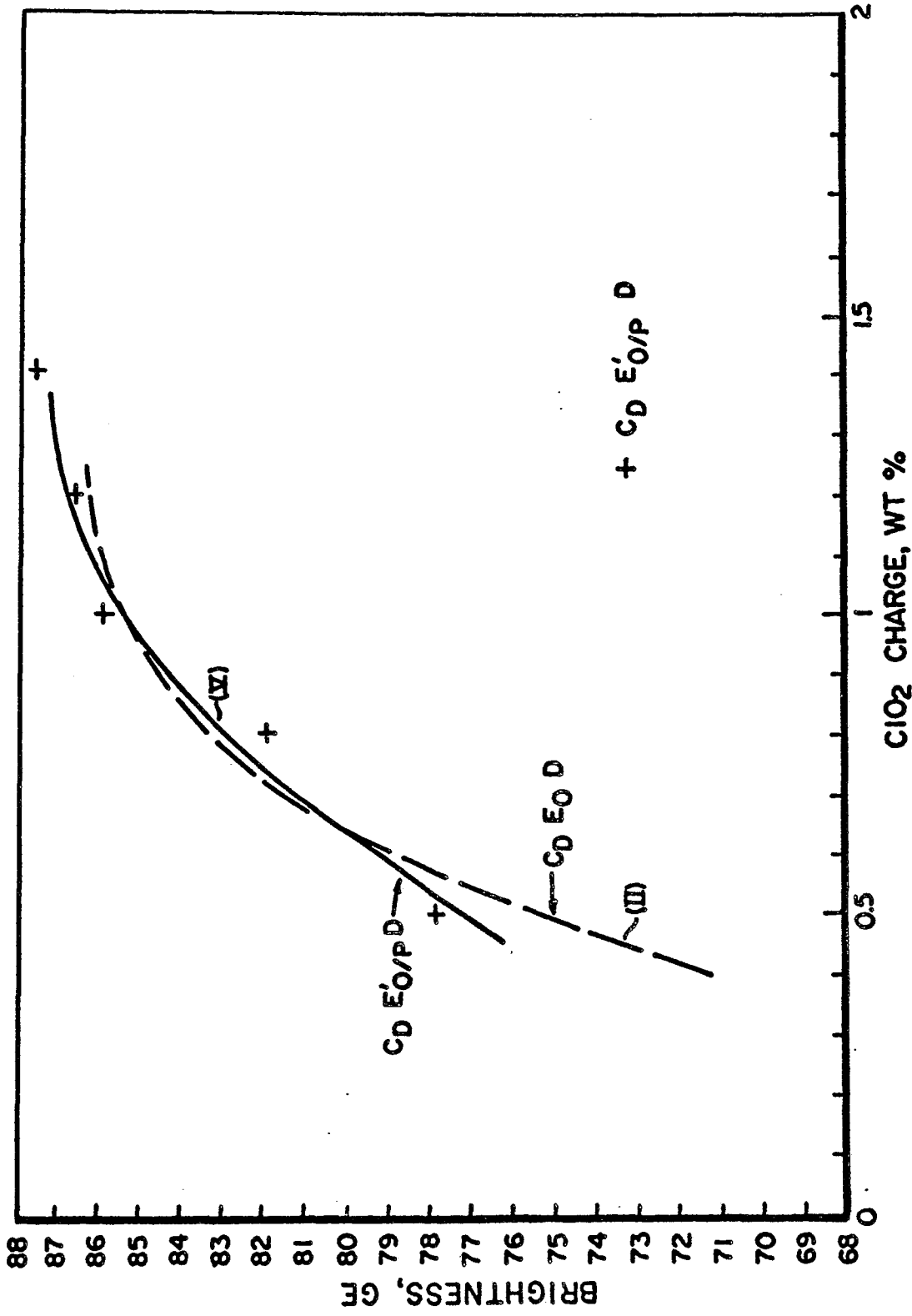


FIG. 8

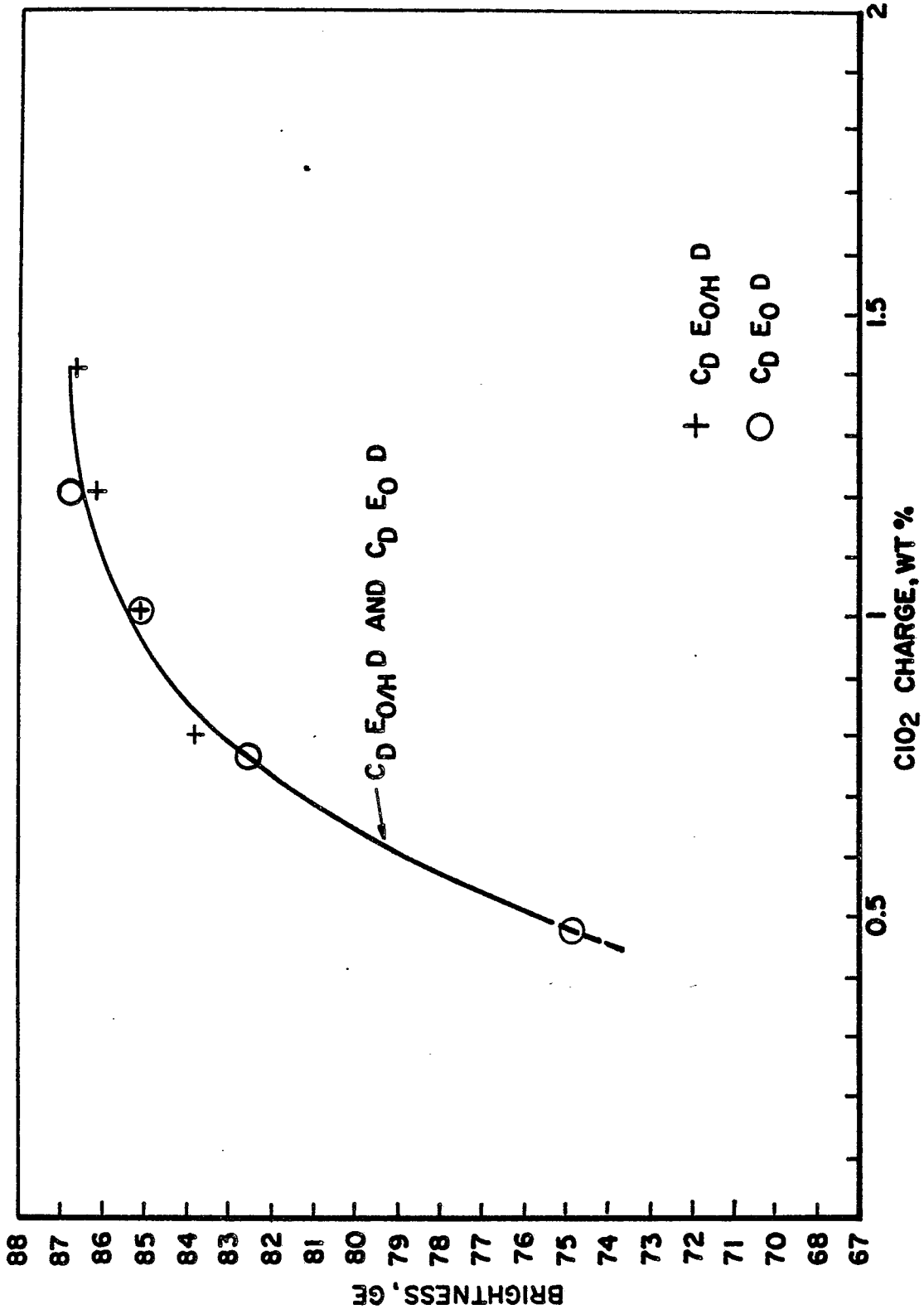


FIG. 9