



(86) Date de dépôt PCT/PCT Filing Date: 2007/11/13
 (87) Date publication PCT/PCT Publication Date: 2008/05/22
 (45) Date de délivrance/Issue Date: 2013/03/19
 (85) Entrée phase nationale/National Entry: 2009/05/08
 (86) N° demande PCT/PCT Application No.: US 2007/023771
 (87) N° publication PCT/PCT Publication No.: 2008/060519
 (30) Priorité/Priority: 2006/11/15 (US11/599,848)

(51) Cl.Int./Int.Cl. *D21C 9/10* (2006.01)
 (72) Inventeur/Inventor:
 YIN, CAIFANG, US
 (73) Propriétaire/Owner:
 INTERNATIONAL PAPER COMPANY, US
 (74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : PROCÉDE DE BLANCHIMENT AMÉLIORÉ AVEC AU MOINS UNE ÉTAPE D'EXTRACTION
 (54) Title: AN IMPROVED BLEACHING PROCESS WITH AT LEAST ONE EXTRACTION STAGE

(57) **Abrégé/Abstract:**

An improved bleaching process for bleaching pulp having at least one Eop stage or Ep stage which comprises subjecting the pulp to a Q stage in which the pulp is treated with a chelating agent at a pH of from greater than 2.5 to less than 7 followed by interstage washing prior to treating the pulp in the Eop or Ep stage. Q stage washing can be at any stage in the process provided that Q stage occurs prior to Eop or Ep stage. For example, Q stage washing may occur after brownstock washing at prior to any delignification stage. Q stage washing can also occur after earlier delignification stages or an oxygen delignification stage or a Do delignification stage. Q stage washing immediately preceding the Eop or Ep stage, or can be separated from these stages by one or more other stage.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 May 2008 (22.05.2008)

PCT

(10) International Publication Number
WO 2008/060519 A3

(51) International Patent Classification:
D21C 9/10 (2006.01)

(21) International Application Number:

PCT/US2007/023771

(22) International Filing Date:

13 November 2007 (13.11.2007)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11/599,848 15 November 2006 (15.11.2006) US

(71) Applicant (for all designated States except US): **INTERNATIONAL PAPER COMPANY** [US/US]; 6400 Poplar Avenue, Memphis, TN 38197 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **YIN, Caifang** [US/US]; 4837 Hampton Pond Lane, Mason, OH 45040 (US).

(74) Agents: **STEWART, Richard, C.** et al.; International Paper Company, 6285 Tri-Ridge Boulevard, Loveland, OH 45140 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH,

CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(88) Date of publication of the international search report:

14 August 2008

(54) Title: AN IMPROVED BLEACHING PROCESS WITH AT LEAST ONE EXTRACTION STAGE

(57) Abstract: An improved bleaching process for bleaching pulp having at least one Eop stage or Ep stage which comprises subjecting the pulp to a Q stage in which the pulp is treated with a chelating agent at a pH of from greater than 2.5 to less than 7 followed by interstage washing prior to treating the pulp in the Eop or Ep stage. Q stage washing can be at any stage in the process provided that Q stage occurs prior to Eop or Ep stage. For example, Q stage washing may occur after brownstock washing at prior to any delignification stage. Q stage washing can also occur after earlier delignification stages or an oxygen delignification stage or a Do delignification stage. Q stage washing immediately preceding the Eop or Ep stage, or can be separated from these stages by one or more other stage.

WO 2008/060519 A3

AN IMPROVED BLEACHING PROCESS WITH AT LEAST ONE EXTRACTION**STAGE****FIELD OF THE INVENTION**

5

This invention relates to the bleaching of lignocellulosic pulp. More particularly, the invention relates to improvements in pulp bleaching.

BACKGROUND OF THE INVENTION

10

Wood is composed of two main parts, namely, a fibrous carbohydrate or cellulosic portion and a non-fibrous portion comprising a complex chemical, commonly referred to as lignin.

For use in papermaking processes wood must first be reduced to pulp, which can be defined as wood fibers capable of being slurried or suspended and then deposited as a screen to form a sheet. The methods employed to accomplish this pulping usually involve either physical or chemical treatment of the wood, or perhaps some combination of the two processes, to alter its chemical form and to give desired paper properties.

In chemical pulping, the wood chips are digested with chemical solutions to solubilize a portion of the lignin and the effect is removal of the lignin. The more usual of these digestive procedures are the sulfite, sulfate or Kraft, soda and modified sulfite processes.

After the wood has been digested, the resulting material is generally a darkly colored cellulose fiber. The dark color is attributable to the fact that not all of the lignin has been

removed during digestion and the remaining lignin has been chemically modified. This dark pulp is commonly referred to as unbleached pulp. It may pass directly to the papermaking operation if the paper color is unimportant or otherwise, the unbleached lignocellulosic pulps are bleached.

Bleaching is a term applied to a semi-chemical or chemical step in which the pulp is treated with
5 an active bleaching agent, such as chlorine, chlorine dioxide, ozone, oxygen, hydrogen peroxide, peroxy acids, enzymes, or a mixture thereof, at a controlled time, temperature, and pH. The desired outcome of these reactions is to brighten the pulp to ever-higher levels of brightness.

Pulp bleaching is most often a multi-stage process employing chlorine or chlorine-containing compounds such as calcium hypochlorite, sodium hypochlorite and chlorine dioxide.

10 The chlorine bleaching of lignocellulosic pulps are the processes well known in the art.

In a typical bleach plant, pulp is subjected to a plurality of bleaching, caustic extraction and washing operations to result in bleached, purified and washed pulp of the required brightness and purification. The pulp is then discharged from the bleach plant for passage to a pulp dryer to provide dried pulp, and then directly to an on-site paper mill.

15 The bleach plant may employ any convenient bleaching sequence such as $D_0EopD_1D_2$, OD_0EopD_1 , $OZEopD_1P$, CED or D_0EC . For example, D_0 represents initial delignification with chlorine dioxide solution and E represents alkaline extraction with caustic (in the presence of oxygen and hydrogen peroxide in the case of Eop), C represents reaction with elemental chlorine in acidic medium, Z is ozone, O denotes bleaching with oxygen, P denotes bleaching with
20 hydrogen peroxide, and D_1 and D_2 are first and second bleaching stages employing chlorine dioxide. Typically, the pulp is washed after each bleaching and each caustic extraction operation.

SUMMARY OF THE INVENTION

One aspect of this invention relates to an improved bleaching process for bleaching pulp having at least one Eop stage or Ep stage which comprises subjecting the pulp to a Q stage in which the pulp is treated with a chelating agent at a pH of from greater than 2.5 to less than 7 followed by
5 interstage washing prior to treating the pulp in the Eop or Ep stage.

Another aspect of this invention relates to an improved bleaching process for bleaching pulp comprising a bleaching sequence selected from the group of the formula:

-QEop- or -QEp-

or a combination thereof, with interstage washing after the Q stage, wherein:

10 Q is a stage in which a pulp is treated with a chelating agent at a pH of from greater than 2.5 to less than 7;

Eop is an extraction stage in which pulp is treated with a composition comprising oxygen, base, and peroxide; and

15 Ep is an extraction stage in which pulp is treated with a composition comprising base and peroxide.

Yet another aspect of this invention relates to an improved bleaching process for bleaching pulp comprising a bleaching sequence selected from the group of the formula:

-D_oQEop- or -D_oQEp-

20 or combination thereof, without interstage washing between D_o and Q stages and with interstage washing after the Q stage, wherein:

Q, Eop and Ep are as defined above; and

D₀ is a delignification stage in which pulp is treated with an agent comprising chlorine dioxide preferably no or substantially no elemental chlorine dioxide (ECF).

The process of the present invention provides one or more advantages over prior processes for brightening bleached pulps. For example, advantages of some of the embodiments of the process of this invention include 1) reduction of bleaching chemicals such as, ClO₂, H₂O₂, NaOH, H₂SO₄ or any combination of the foregoing, 2) reducing the bleaching cost, 3) low capital requirement, 4) high pulp brightness and brightness stability, 5) higher pulp viscosity, 6) improved bleached plant performance and stability, 7) reduction in filtrate AOX or 8) a combination of two or more of the aforementioned advantages. Some embodiments of this invention may exhibit one of the aforementioned advantages while other preferred embodiments may exhibit two or more of the foregoing advantages in any combination.

In this process, less peroxide is required in the bleaching Eop or Ep stage as compared to conventional bleaching process that do not include a Q stage followed by a washing stage to obtain comparable levels of brightness or higher brightness can be obtained using the same amount of peroxide in the Eop or Ep stage. The present bleaching sequence facilitates the pulp metal profile prior to the Eop or Ep stage to be more conducive to peroxide treatment by selectively removing detrimental metals such as Mn, Fe, and Cu while maintaining beneficial alkaline earth metals such as Mg and Ca. For example, the ratio of the Mg and Ca to Mn/Fe/Cu is greatly increased with the D₀/Q treatment when compared with the conventional D₀ treatment given the same specified conditions.

DETAILED DESCRIPTION OF THE INVENTION

While this invention is susceptible of embodiment in many different forms, there is shown and described in drawing, figures, and examples and will herein be described in detail preferred embodiments of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspect of the invention to the embodiments illustrated.

One aspect of this invention relates to an improved bleaching process for bleaching pulp having at least one Eop stage or Ep stage which comprises subjecting the pulp to a Q stage in which the pulp is treated with a chelating agent at a pH of from greater than 2.5 to less than 7 followed by interstage washing prior to treating the pulp in the Eop or Ep stage.

In the preferred embodiment of this invention, the Q stage and following interstage washing can be at any stage in the process provided that Q stage followed by a washing stage or an oxygen delignification stage occurs prior to Eop or Ep stage. For example, the Q stage may occur after brownstock washing and at prior to any delignification stage. Thereafter, the pulp can be washed immediately following the Q stage or at any subsequent point prior to the Eop or Ep stage or for example, prior to or after a subsequent D₀ delignification stage. The Q stage can also occur after earlier delignification stages as for example an oxygen delignification stage and/or a D₀ delignification stage followed by a subsequent interstage washing prior to the Eop or Ep stage. Q stage with interstage washing can be immediately preceding the Eop or Ep stage, or can be separated from these stages by one or more other stages.

Another aspect of this invention relates to an improved bleaching process for bleaching pulp comprising a bleaching sequence selected from the group of the formula:

-QEop- or -QEp-

or a combination thereof, with interstage washing wherein Q, Eop or Ep are defined as above.

5 Chelating agents used in the Q stage can be varied widely depending on their effectiveness to bind and hold on (chelate) the peroxide detrimental metals mainly Mn at the pH requirement of the Q stage. Any conventional chelating agents can be used for the practice of this invention. The selection will be therefore dictated by the effectiveness of the chelants under use conditions. For example useful chelating agents include but are not limited to diethylene triamine pentaacetic acid (DTPA), to aminopolycarboxylic acids (APCA), ethylenediaminetetraacetic acid (EDTA),
10 nitrilotriacetic acid (NTA), phosphoric acids, ethylenediaminetetramethylene-phosphonic acid (EDTMP), diethylenetriaminepentamethylenephosphonic acid (DTPMP), nitrilotrimethylenephosphonic acid (NTMP), polycarboxylic acids, gluconates, citrates, polyacrylates, and polyaspartates or any combination thereof. Mixtures of thermodynamic and
15 kinetic controlling chelating agents (e.g. citrates, keto acids, gluconates, heptagluconates, phosphates, and phosphonates) also work well in reducing the content of free heavy metal ions in the paper to acceptable levels. Preferred chelating agents are DTPA or EDTA and the more preferred chelating agent is DTPA.

The pH of the Q stage is in the range from greater than 2.5 to about 7.0. Any pH within this
20 range can be used. For example, the pH can be as high as about 4, 5, or 6 and as low as about 3.0 to about 7.0. In the preferred embodiments of the invention, the pH is from about 4.0 to about 7.0. In

the more preferred embodiments of the invention, the pH is from about 5 to about 6 and in the most preferred embodiments of the invention, the pH is from about 5.0 to about 5.5.

The consistency (CSC) of the pulp in the Q stage may vary widely and any consistency that provides the desired increase in pulp brightness may be used. The pulp may be bleached
5 under low consistency conditions (i.e. from about 3 % to about 6 % based on the total weight of the mixture of pulp and bleaching chemicals), medium consistency conditions (i.e. from about 8 % to about 14 % based on the total weight of the mixture of pulp and bleaching chemicals) or high consistency conditions (i.e. from about 20 % to about 30 % based on the total weight of the mixture of pulp and bleaching chemicals). The consistency is preferably from about 3.5% to
10 30%, more preferably from about 5.5% to 20%, and most preferably from about 6.0% to about 10%.

The Q stage retention times will vary widely and times used in conventional bleaching stages may be used. Usually, retention times will be at least about 10 minutes. Retention times are preferably from about 10 min. to about 300 min., and are more preferably from about 15 minutes to
15 about 120 min. and most preferably from about 20 min. to about 80 min.

Similarly, The Q stage bleaching temperatures employed in the critical bleaching stage may vary widely and temperatures employed in conventional bleaching stages may be used. For example, useful temperatures can be as low as about 25 °C or lower and as high as about 100 °C or higher. In the process of this invention, the bleaching temperature is usually from about 25 °C to
20 about 120 °C, preferably from about 40 °C to about 100 °C, more preferably from about 60 °C to about 90 °C and most preferably from about 40 °C to about 50 °C.

After Q stage the pulp is immediately washed or is washed at some subsequent point in the process prior to the Ep or Eop stage. Pulp washing after the Q stage removes all the or a portion of the chelated metals to protect peroxide used in the subsequent Ep or Eop stage. In the preferred embodiment of the invention at least about 50% of the chelated metals are removed and in the more preferred embodiments at least about 75% of the chelated metals are removed by washing after the Q stage. In the most preferred embodiment of the invention all or substantially all of the chelated metals are removed by washing after the Q stage. In the preferred embodiment of the invention, interstage washing is immediately after the Q stage.

After the washing stage, the pulp is subjected to extraction in an Eop or Ep stage. The Eop stage refers to alkaline extraction of pulp with oxygen (O) and hydrogen peroxide (P), and Ep stage refers to alkaline extraction of pulp with hydrogen peroxide (P). Conventional processes and apparatus can be used in the Ep or Eop stage. See for example "Pulp Bleaching Principles and Practice of Pulp Bleaching" Carlton W. Dence and Douglas W. Reeve, TAPPI Press, 1996 and references cited therein.

However, one of the advantages of a preferred embodiment of this invention is the reduction of bleaching chemicals such as H_2O_2 , NaOH, or combination thereof in the Eop and/ or Ep stages as compared to the same or substantially the same bleaching processes which do not include the Q stage. For example, the reduction in the amount of H_2O_2 is typically at least about 10 %, preferably at least about 60 %, more preferably from about 15 % to about 50 % and most preferably from about 20 % to about 40 % less than the amount of H_2O_2 used in the same or

substantially the same bleaching processes which do not include the Q stage followed by interstage washing to obtain the same or substantially level of pulp brightness in the Do stage.

In the most preferred embodiments of the invention when hydrogen peroxide is used as a bleaching agent in the Eop or Ep extraction stage. The amount of hydrogen peroxide in the bleaching liquor is preferably from about 15 to about 200 pounds per ton of pulp on a dry basis. The hydrogen peroxide is conventionally obtained from suppliers as a mixture of 50 % water and 50 % hydrogen peroxide on a weight basis, but other proportions of water and hydrogen peroxide can be used, provided they are equivalent to from 10 to 200 pounds of H₂O₂ chemical. These amounts of hydrogen peroxide can be applied to the methods of brightening mechanical as well as chemical pulps according to the present invention. The amount of extraction agent oxidant used (e.g. hydrogen peroxide and chlorine dioxide) used in the practice of the process of this invention can vary widely and any amount sufficient to provide the desired degree of brightness can be used. The amount of bleaching agent used is usually at least about 0.2 % based on the dry weight of the pulp. Preferably the amount of bleaching agent is from about 0.5 % to about 1 %, more preferably from about 0.5 % to about 0.8 % and most preferably about 0.5-0.8 % on the aforementioned basis.

Another advantage a preferred embodiment of this invention is the reduction of AOX resulting from the Eop and/ or Ep stages as compared to the same or substantially the same bleaching processes which do not include the Q stage. For example, the reduction in the amount of AOX is typically at least about 20 %, preferably at least about 30 %, more preferably from about 10 % to about 50 % and most preferably from about 20 % to about 30 % less than the amount of AOX

produced in the same or substantially the same bleaching processes which do not include the Q stage to obtain the same or substantially level of pulp brightness in the Eop and/or Ep stages.

In addition, the Eop or Ep pulp brightness and viscosity were higher than those treatments without Q stage, which indicates the positive impact of Q treatment on the peroxide efficiency and selectivity in the Ep stage. For example, the viscosity is typically at least about 5 %, preferably at least about 10 %, more preferably from about 5 % to about 15 % and most preferably from about 5 % to about 10 % greater than the viscosity of the pulp made by the same or substantially the same bleaching processes which do not include the Q stage. For example, the brightness is typically at least about 2 %, preferably at least about 10 %, more preferably from about 5 % to about 15 % and most preferably from about 7 % to about 10 % greater than the brightness of the pulp made by the same or substantially the same bleaching processes which do not include the Q stage.

In the preferred embodiment of this invention a D₀ delignification or other oxidative delignification stages as for example with O₂, peracetic acid and the like is applied prior to the QEop or QEp stage.

Conventional process parameters employed in these oxidative extraction stage can be described in, for example "Pulp Bleaching Principles and Practice of Pulp Bleaching" Carlton W. Dence and Douglas W. Reeve, TAPPI Press, 1996 and references cited therein. Accordingly, they will not be described in greater detail.

In the preferred embodiment of this invention in which a prior D₀ extraction stage is used, the pH in the D₀ stage of the present invention is higher than the pH of the conventional D₀ bleaching stage. The advantages of higher pH are higher brightness, less AOX formation,

elimination of H₂SO₄ addition, associated BaSO₄ scale formation or a combination of two or more thereof. The pH of the D₀ stage is preferably in the range from greater than 3 to about 6. Any pH within this range can be used. For example, the pH can be as high as about 4, 5, or 6 and as low as about 2.5 to about 3. In the preferred embodiments of the invention, the pH is from about 3 to about 5 6. In the more preferred embodiments of the invention, the pH is from about 4 to about 6 and in the most preferred embodiments of the invention, the pH is from about 4.5 to about 5.5.

However, one of the advantages of a preferred embodiment of this invention is the reduction of bleaching chemicals such as ClO₂, H₂SO₄, or combination thereof in the D₀ stage as compared to the same or substantially the same bleaching processes which do not include the Q 10 stage. For example, the reduction in the amount of ClO₂ is typically at least about 5 %, preferably at least about 10 %, more preferably from about 5 % to about 20 % and most preferably from about 10 % to about 20 % less than the amount of ClO₂ used in the same or substantially the same bleaching processes which do not include the Q stage to obtain the same or substantially level of pulp brightness in the E_{op} and or E_p stages. The amount of extraction agent used (e.g. sodium 15 hydroxide, magnesium hydroxide, potassium hydroxide, ect.) used in the practice of the process of this invention can vary widely and any amount sufficient to provide the desired lignin extraction efficiency and the desired degree of brightness can be used. The amount of caustic used is usually at least about 0.5 % based on the dry weight of the pulp. Preferably the amount of bleaching agent is from about 1 % to about 8%, more preferably from about 1.5 % to about 3 % 20 and most preferably about 1-2 % on the aforementioned basis.

Another advantage a preferred embodiment of this invention is the reduction of AOX resulting from the D₀ stage as compared to the same or substantially the same bleaching processes which do not include the Q stage. For example, the reduction in the amount of AOX is typically at least about 20 %, preferably at least about 30 %, more preferably from about 10 % to about 50 % and most preferably from about 20 % to about 30 % less than the amount of AOX produced in the same or substantially the same bleaching processes which do not include the Q stage to obtain the same or substantially level of pulp brightness in the D₀ stage.

In the most preferred embodiments of the invention, the amount of chlorine dioxide in the D₀ extraction stage liquor is preferably from about 10 to about 200 pounds per ton of pulp on a dry basis. The chlorine dioxide is conventionally obtained from suppliers as a mixture of 90 % water and 10 % chlorine dioxide on a weight basis, but other proportions of water and chlorine dioxide can be used, provided they are equivalent to from 10 to 200 pounds of ClO₂ chemical. These amounts of chlorine dioxide can be applied to the methods of brightening mechanical as well as chemical pulps according to the present invention.

In addition, in the D₀ stage the brightness is higher than those treatments without Q stage, which indicates the positive impact of Q treatment on the chlorine dioxide efficiency and selectivity in the D₀ stage. For example, the brightness is at least about 1 %, preferably at least about 2 %, more preferably from about 3 % to about 5 % and most preferably from about 6 % to about 7 % greater than the brightness of the pulp made by the same or substantially the same bleaching processes which do not include the Q stage.

In addition to the Q stage followed by a washing stage prior to the Ep or Eop stage or ,
 QEop, QEp, D₀QEop or D₀QEp, sequence in the preferred embodiment of the invention, the other
 sequences are, for example, D₀EopD₁, OD₀EopD₁, D₀EopD₁D₂, OD₀EopD₁D₂, D₀EopD₁EpD₂,
 OD₀EopD₁EpD₂, DEopD₁P. bleaching process of this invention may include other bleaching stages
 5 as for example bleaching with Cl₂, peroxy acids, chlorine dioxide, ozone and the like, and
 extraction stages such as extraction with oxygen, ozone, borohydride, chlorine dioxide and the like
 in the presence other bases such as Mg(OH)₂. Illustrative of such bleaching processes are O(D₀/C
 Q)Eop, (D₀Q)EopD, (D₀Q)EOPDD, (D₀Q)EopED, (D₀Q)EDEpEopD, ZEQ(Eop)D, ZQ(Eop)D,
 D₀QEopZ(Eop) , D₀QEopZD(ZD), D₀Q(Eop)D(ZD), D₀Q(Eop)PP, D₀Q(Eop)DZ, DoQEopD₁,
 10 ODoQEopD₁, DoQEopD₁D₂, ODoQEopD₁D₂, DoQEopD₁EpD₂, ODoQEopD₁EpD₂, DQEopD₁P
 and the like in which D is as described above and Z is ozone, E is extraction in the presence of base,
 O is oxygen, P is peroxide, D/C is a mixture of chlorine dioxide and elemental chlorine and two or
 more symbols in parenthesis indicate an absence of an intermediate washing stage. The Eop, Ep,
 and Do are defined above herein. The processes and apparatus used in the D, Z, E, O, P, D/C are
 15 conventional and there are well known in art. See for example, "Pulp Bleaching Principles and
 Practice of Pulp Bleaching" Carlton W. Dence and Douglas W. Reeve, TAPPI Press, 1996 and
 references cited therein.

The plant source of pulp for use in this invention is not critical and may be any fibrous
 plant which can be subjected to chemical pulp bleaching. Examples of such fibrous plants are
 20 trees, including hardwood fibrous trees such as aspen, eucalyptus, maple, birch, walnut, acacia
 and softwood fibrous trees such as spruce, pine, cedar, including mixtures thereof. In certain

embodiments, at least a portion of the pulp fibers may be provided from non-woody herbaceous plants including, but not limited to, kenaf, hemp, jute, flax, sisal, or abaca although legal restrictions and other considerations may make the utilization of hemp and other fiber sources impractical or impossible. The source of pulp for use in the practice of this invention is
5 preferably hardwood and softwood fibrous trees, more preferably Eucalyptus, Spruce and Aspen and is most preferably Aspen and Spruce.

The pulp used in the process of this invention can be obtained by subjecting the fibrous plant to any chemical pulping process. Following the wood digestion process, pulp is separated from the spent pulping liquor. The spent pulping liquor is then recovered and regenerated for
10 recycling. The pulp is then bleached and purified in a bleach plant operation.

The pulp of this invention can also be used in the manufacture of paper and packaging products such as printing, writing, publication and cover papers and paperboard products. Illustrative of these products and processes for their manufacture are those described in USP Nos. 5,902,454 and 6,464,832.

15 For example, in the paper or paperboard making process, the bleached pulp of this invention or pulp mixtures comprising the bleached pulp of this invention is formulated into an aqueous paper making stock furnish which also comprises one or more additives which impart or enhance specific sheet properties or which control other process parameters. Illustrative of such additives is alum which is used to control pH, fix additives onto pulp fibers and improve
20 retention of the pulp fibers on the paper making machine. Other aluminum based chemicals which may be added to furnish are sodium aluminate, poly aluminum silicate sulfate and poly

aluminum chloride. Other wet end chemicals which may be included in the paper making stock furnish for conventional purposes are acid and bases, sizing agents, dry-strength resins, wet strength resins, fillers, coloring materials, retention aids, fiber flocculants, defoamers, drainage aids, optical brighteners, pitch control chemicals, slimicides, biocides, specialty chemicals such as corrosion inhibitors, flame proofing and anti-tarnish chemicals, and the like.

The aqueous paper making stock furnish comprising the bleached pulp and the aluminum based compounds is deposited onto the forming wire of a conventional paper making machine to form a wet deposited web of paper or paperboard and the wet deposited web of paper or paperboard is dried to form a dried web of paper or paperboard. Paper making machines and the use of same to make paper are well known in the art and will not be described in any great detail. See for example, Pulp and Paper Chemistry and Handbook for Pulp & Paper Technologies, supra. By way of example, the aqueous paper making stock furnish containing pulp, aluminum based and other optional additives and usually having a consistency of from about 0.3% to about 1% is deposited from the head box of a suitable paper making machine as for example a twin or single wire Fourdrinier machine. The deposited paper making stock furnish is dewatered by vacuum in the forming section. The dewatered furnish is conveyed from the forming section to the press section on specially-constructed felts through a series of roll press nips which removes water and consolidates the wet web of paper and thereafter to the dryer section where the wet web of paper is dried to form the dried web of paper of this invention. After drying, the dried web of paper may be optionally subjected to several dry end operations such as and various surface treatments such as coating, and sizing and calendering.

The paper manufactured in accordance with this invention can be used for conventional purposes. For example, the paper is useful as printing paper, publication paper, newsprint and the like.

The present invention is described in more detail by referring to the following examples and comparative examples which are intended to more practically illustrate the invention and not to be a limitation thereon.

Example 1

The pulp was made from southern hardwood cooked by the Kraft process. The unbleached pulp had 10.1 Permanganate number, 26% brightness, and 24 cP viscosity. The pulp was bleached in lab with a D₀EpD and D₀/QEpD three-stage ECF (elemental chlorine free) bleaching sequence.

Each bleaching stage was conducted in sealed plastic bags at the specified conditions (consistency, pH, temperature, and retention time). All pulp samples were preheated to the bleaching temperature, and all the chemicals were added sequentially and mixed thoroughly with the pulp before addition of another chemical. The chemical addition sequence in the D stages are deionized water, acid or caustic (whatever needed for pH control), and ClO₂. In the Eop stage, the chemical addition sequence was deionized water, caustic, H₂O₂, and O₂.

After completing each bleaching stage, the pulp was squeezed to collect filtrate for pH, residual, and COD measurement. The pulp was repulped at 1% consistency with deionized water and dewatered on a Buchner funnel and repeat a couple of time to simulate a pulp washing stage in mills. The washed pulp was analyzed for brightness, viscosity, and pulp dirt. All the filtrate

and pulp analysis was done with the standard published procedures understood by all the people working in the field.

Table 1 shows the bleaching results and conditions of hardwood pulp on two control ECF bleaching sequences on the left two columns and two D/Q based ECF bleaching sequences on the

5 two right columns.

Table 1

Table 1. Hardwood D/Q Based ECF Bleaching Study				
Do Versus D/Q Technology				
Bleach No	1	2	3	4
Sequence	D_{Control}EpD	D_{Control}EpD	D/QEpD	D/QEpD
Do Stage Conditions: 65 °C, 30 min, 4% Consistency (CSC)				
ClO ₂ , %	0.8	1.1	0.8	1.1
H ₂ SO ₄ , %	1.1	0.8	0	0
pH	2.52	2.49	5.29	4.31
ClO ₂ res., gpl	0	0	0.13	0.08
Brightness, %	41.8	48.2	39.8	51.1
Q Stage Conditions: 60 °C, 30 min, 4% CSC				
DTPA, %	N/A	N/A	0.15	0.15
pH	N/A	N/A	5.70	4.44
Brightness, %	N/A	N/A	40.5	51.6
Ep Stage Conditions: 80 °C, 10% CSC, 60 min, 0.5% H₂O₂				
NaOH, %	1.2	1.2	1	1
pH	10.99	11.14	11.09	11.0
H ₂ O ₂ res., %	0.006	0.003	0.184	0.22
Brightness, %	63.1	66.8	66.3	73.2
P#	3.4	2.7	3.6	2.7
Viscosity, cP	18.5	17.8	21.0	20.4
D1 Stage Conditions: 120 min, 10% CSC, 75 °C				
ClO ₂ , %	0.8	0.5	0.5	0.5
NaOH, %	0.15	0.1	0.1	0.1
pH	3.22	4.05	4.94	4.19
ClO ₂ res., gpl	0	0	0	0
Brightness, %	81.4	82.3	82.5	84.5
Viscosity, cPs	17.5	15	19.7	19.2
Dirt, ppm	0	0	0	0

Two control ECF sequences (Bleach Nos. 1 & 2) were performed by varying the ClO₂ usage distribution in the Do and D₁ stage while maintaining the constant total ClO₂ charge. A final pulp brightness of 82% was achieved. Two D/Q based ECF bleaching sequences (Bleach No. 3 & 4) were designed with a varying Do stage ClO₂ charge in order to match the performance (final pulp brightness) of the control sequences. In the D/Q stage, the organic chelant, DTPA, was added to the pulp slurry after the Do stage “as is” without washing. The DTPA dosage was 0.15% and the retention time in the Q stage was 30 min. Bleach No. 3 and No. 4 had no H₂SO₄ addition. The Do stage pHs were 5.44 and 4.11 at 0.8% and 1.1% ClO₂ charges respectively. The Q stage pHs were 5.91 and 4.49, respectively, for 0.8% and 1.1% ClO₂ charges in the Do stage.

As shown in Table 1, the Ep pulp brightness and viscosity after D/Q treatment in Bleach No 3 and No 4 were higher than those of the lab control Ep pulps in control Bleach No. 1 and 2 at the same Do ClO₂ charges, indicating the positive impact of Q treatment on the peroxide efficiency and selectivity in the Ep stage. The brightness and viscosity advantages of the D/QEp pulps over the DEp pulps are maintained after the D₁ stage. Comparing the results in Control Bleach Nos. 1 & 2 with those of Bleach No. 3 shows that D/Q based ECF Bleach No. 3 produces the same brightness pulp and 2-3.5 points higher pulp viscosity as the control ECF Bleach Nos. 1 and 2 with 0.3% less ClO₂ charge (in the Do stage) and 0.2% NaOH (in the Ep stage). A comparison of Bleach No. 4 with control Bleach Nos. 1 and 2 shows that increasing the Do ClO₂ charge in the D/Q stage to the same level as the control Do stage increased final pulp brightness while maintaining 3 points higher pulp viscosity (Bleach No. 4 Control). Overall, the D/QEpD

sequence (Bleach No. 3) requires significantly lower ClO_2 , NaOH, and H_2SO_4 charges than those of the control (Bleach Nos. 1 and 2). The net results are that addition of 3 lb/t DTPA in the Q stage (Bleach No. 3) was translated to a 6 lb/t ClO_2 and 22 lb/t H_2SO_4 decrease in the Do stage and a 4 lb/t NaOH decrease in the Ep stage (Bleach No. 2). The D/QEpD bleached pulp also had 5 2-3 cPs higher viscosity than the control.

Example 2

Using a standard analytical procedure, series of experiments were carried out to determine the amount of Mg, Mn, and Ca present in unbleached pulp and pulp resulting from the Do and D/Q stages of Bleach Nos. 2 and 3. The results are set forth herein the following table 2.

Table 2

Table 2. HW Pulp Study			
	Unbleached	Do Bleach No. 2 (as in Table 1)	D/Q Bleach No. 3 (as in Table 1)
Mn, ppm	31	2.84	1.86
Mg, ppm	267	24.3	85
Ca, ppm	4155	384	1680

As shown in Table 2, the ratio of the beneficial metals, Mg and Ca, to detrimental metals, Mn, are greatly increased with the D/Q treatment (Bleach No.3) as compared with the 15 conventional D treatment (Bleach No.2). This is the basis of the observed bleaching efficiency and selectivity improvement, manifested by the improved viscosity and brightness at significantly lower bleaching chemical cost.

A surprising discovery was the fact with respect to conducting Do stage at pH 4.5-6 without adversely affecting pulp viscosity which would have otherwise occurred in the

conventional Do stage. In fact, the D/Q pulp viscosity was significantly higher than that of the Do pulp.

Example 3

Using the procedure of Example 1, a series of experiment were carried out to determine the effect of D/Q pH and interstage washing on pulp brightness. The process results and conditions are set forth in the following Table 3.

Table 3

Table 3. Hardwood D/Q Based ECF Bleaching Study				
Effect of Do pH and Washing				
Bleach No	5	6	7	8
Sequence	D/Q*	D/Q*	D/Q**	D/Q**
Do Stage Conditions: 65 °C, 30 min, 4% Consistency (CSC)				
ClO ₂ , %	<i>0.8</i>	<i>1.1</i>	0.8	1.1
H ₂ SO ₄ , %	<i>0</i>	<i>0</i>	1.1	0.8
pH	<i>5.44</i>	<i>4.11</i>	2.63	2.71
ClO ₂ res., gpl	<i>0.11</i>	<i>0.026</i>	0	0
Brightness, %	<i>39.7</i>	<i>48.9</i>	42.0	48.7
Q Stage Conditions: 60 °C, 30 min, 4% CSC				
DTPA, %	<i>0.2</i>	<i>0.2</i>	0.1	0.1
pH	<i>5.91</i>	<i>4.49</i>	4.34	4.39
Brightness, %	<i>42.2</i>	<i>51.0</i>	42.4	48.4
Ep Stage Conditions: 80 °C, 10% CSC, 60 min, 0.5% H₂O₂				
NaOH, %	<i>1</i>	<i>1</i>	1.2	1.2
pH	<i>11.03</i>	<i>11.07</i>	11.11	11.24
Brightness, %	<i>66.4</i>	<i>73.4</i>	65.3	70.1
P#	<i>3.8</i>	<i>2.9</i>	3.4	2.9
Viscosity, cP	<i>20.4</i>	<i>19.5</i>	19.3	18.0
D/Q* - No interstage washing between D and Q stage				
D/Q** - With Interstage washing between D and Q stage				

10

As shown in Table 3, the Do stages in Bleach No 5 and No 6 were conducted at 5.44 and 4.11 pH for 0.8% and 1.1% ClO₂ charges without H₂SO₄ addition and the Do pulp was

subsequently treated with a Q stage at pH 5.91 and 4.11, respectively without washing of the Do pulp. In comparison, the Do stages in Bleach No. 7 and No 8 were conducted at 2.63 and 2.71 pH for 0.8% and 1.1% ClO₂ charges, respectively, by H₂SO₄ addition and the subsequent Q stages at pH 4.34 and 4.39. Washing was performed after the low pH Do delignification to
5 manage the Q stage toward 5 optimum pH.

The results in Table 3 show that the pulp brightness is higher at higher Do and Q stage pH treatment (Bleach No 5 and No 6) than at lower Do and Q treatment pH (Bleach No 7 and No 8). This indicates that the best pH for D/Q treatment with DTPA chelant is to control both D and Q stages toward a pH of about 5.

Example 4

10 Using the procedure of Example 1, a series of experiment were carried out to determine the effect of DTPA charge on the delignification efficiency. The process results and conditions are set forth in the following Table 4.

Table 4

Table 4. Hardwood ECF Bleaching Study				
Effect of DTPA Charge				
Bleach No	9	10	11	12
Sequence	D_{Control}	D/Q	D/Q	D/Q
Do Stage Conditions: 65 °C, 30 min, 4% CSC (Consistency), 0.8% ClO₂				
H ₂ SO ₄ , %	1.1	0	0	0
pH	2.66	5.43	5.43	5.43
ClO ₂ res., gpl	0	0.156	0.156	0.156
Brightness, %	42.1	39.3	39.3	39.3
Q Stage Conditions: 60 °C, 30 min, 4% CSC				
DTPA, %	N/A	0.1	0.2	0.3
pH	N/A	5.88	5.78	5.89
Brightness, %	N/A	42.3	42.9	42.2
Ep Stage Conditions: 80 °C, 10% CSC, 60 min, 0.5% H₂O₂				
NaOH, %	1.2	1	1	1
pH	11.06	11.28	11.22	11.21
H ₂ O ₂ res., %	0.008	0.209	0.22	0.214
Brightness, %	63.3	66.9	66.7	67.1
P#	3.5	3.8	3.9	3.9
Viscosity, cP	18.0	20.6	20.5	20.4
D1 Stage Conditions: 120 min, 10% CSC, 75 °C				
ClO ₂ , %	0.5	0.5	0.5	0.5
NaOH, %	0.1	0.1	0.1	0.1
pH	4.25	4.86	4.83	4.88
ClO ₂ res., gpl	0	0	0	0
Brightness, %	79.7	82.5	82.5	82.5
Viscosity, cPs	17.5	20.2	19.9	22.0
Dirt, ppm	0	0	0	0

The 2 lb/t (0.1) DTPA is sufficient to produce significant savings in ClO₂, H₂SO₄, and

- 5 NaOH as good as higher DTPA charges.

Example 5

Using the procedure of Example 1, a series of experiment were carried out to determine the effect of the ClO₂ and DTPA addition sequence. The effects of the ClO₂ and DTPA addition

sequence are illustrated in Table 5. The process results and conditions are set forth in the following Table 5.

Table 5

5

Table 5. Hardwood ECF Bleaching Study			
Effect of D and Q Sequence			
Bleach No.	9	13	14
Sequence	D_{Control}	D/Q	Q/D
Do Stage Conditions: 65 °C, 30 min, 4% CSC (Consistency), 0.8% ClO₂			
Q Stage Conditions: 60 °C, 30 min, 4% CSC, 0.15% DTPA			
H ₂ SO ₄ , %	1.1	0	0
D pH	2.66	5.43	3
ClO ₂ res., gpl	0	0.156	0
Brightness, %	42.1	39.3	41
Q pH	N/A	5.78	5.78
Brightness, %	N/A	42.9	27.1
Ep Stage Conditions: 80 °C, 10% CSC, 60 min, 0.5% H₂O₂			
NaOH, %	1.2	1	1.1
pH	11.06	11.22	10.65
H ₂ O ₂ res., %	0.008	0.22	0
Brightness, %	63.3	66.7	62.8
P#	3.5	3.9	3.8
Viscosity, cP	18.0	20.5	17.9
D1 Stage Conditions: 120 min, 10% CSC, 75 °C			
ClO ₂ , %	0.5	0.5	0.5
NaOH, %	0.1	0.1	0.1
pH	4.25	4.83	4.25
ClO ₂ res., gpl	0	0	0
Brightness, %	79.7	82.5	79.8
Viscosity, cPs	17.5	20.0	17.3
Dirt, ppm	0	0	0

As the results from Bleach No. 13 (D/Q) and Bleach No 14 (Q/D) show, the D/Q based ECF bleaching (Bleach No.13) produced higher pulp brightness than Q/D based ECF bleaching (Bleach No.14) at otherwise the same conditions. Bleach No. 9 was served as the control ECF bleaching in this block of bleaches.

10

Example 6

The AOX filtrate from the D/Q filtrate of Bleach Nos. 3 and 4 and Do filtrate Bleach Nos. 1 and 2 were evaluated using the EPA approved AOX analysis procedure. The analysis of the filtrate AOX shows that the AOX concentration in D/Q filtrate was 19.4 ppm as compared with 43.7 mg/l AOX from the Do filtrate. The consistency of both D/Q and D stages are the same. The total filtrate AOX from DEp and D/QEp sequences are 0.97 kg/ton of pulp and 0.45 kg/ton of pulp, respectively. Therefore, conversion of the current Do stage to D/Q stage has a potential to decrease AOX formation from ECF bleaching by about 50%. The reduced AOX formation in D/Q is mainly due to Do (ClO₂) delignification at higher pH with some reduction due to reduced ClO₂ usage in the Do stage.

Example 7

The pulp properties from the DEpD control bleaching in a similar procedure as Bleach No. 1 or 2 in Table 1 and D/QEpD bleaching in a similar procedure as bleach No. 3 in Table 1 were evaluated using the lab standard testing procedures as described below.

Brightness

Approximately 5 grams of pulp is rolled or pressed on a disc and is permitted to completely dry. The brightness is measured on both sides of the brightness pad, at least four readings per side and then the average is calculated. These readings are performed on a GE brightness meter which reads a directional brightness or on an ISO brightness meter which reads a diffused brightness. Both instruments are made by Technidyne Corp.

Viscosity

The viscosity is a measurement used to compare a relative strength property of the pulp. This property is used to determine the percentage of hardwood/softwood for making different grades of paper. A Cannon-Fenske (200) viscometer tube, calibrated for 25 C, is used for testing bleached pulps. The sample size is 0.2000 grams, using 20 ml, 1.0 molar CED and 20ml DI water mixed thoroughly to break down the pulp fiber.

Permanganate Number

The Permanganate Number indicates the amount of lignin that is in the pulp. (The Kappa number is generally used only on the brownstock, while the value for the Permanganate Number is comparative to the bleached pulp.) The procedure for determining the Permanganate Number

10 is:

1. Weigh exactly 1.00 gram sample.
2. Put the sample in a blender with 700 ml DI water and blend about 45 seconds, pour the sample into a battery jar on a stir plate.
3. Add exactly 25 ml of 0.1 N Potassium Permanganate and 25 ml 4N H₂SO₄, starting a
15 timer set for 5 min.
4. When the timer stops, add 6 ml 1 Molar KI and allow it to mix thoroughly to kill the reaction.
5. Titrate to a starch end point with 0.1N Sodium Thiosulfate. Record mls titrated.
6. In 700ml DI water without the pulp sample, use the same reagents and titrate to use as a
20 blank. Using an accurately prepared Potassium Permanganate, the blank should be 25.0

7. Subtract the mls titrated with the sample from the mls titrated for the blank and the result will be the P Number.

Dirt

- Pulp dirt count is done by a visual count of all the dirt spots on the brightness pad and is the size weighted sum of the total dirt spots according to a Tappi temperature rate. The results are shown in the following Table 8.

Table 7

Table 7. Hardwood ECF Bleaching Study			
Pulp Property at 82% Brightness			
Sequence	DEpD	DEpD	D/QEpD
ClO ₂ , %	1.3	1.6	<i>1.3</i>
H ₂ SO ₄ , %	1.1	0.8	<i>0</i>
NaOH, %	1.3	1.3	<i>1.1</i>
H ₂ O ₂ , %	0.5	0.5	<i>0.5</i>
DTPA, %	0	0	<i>0.1</i>
Brightness, %	79.7	82.1	<i>82.5</i>
Viscosity, cPs	17.5	17.1	<i>20</i>
Dirt, ppm	0	0	<i>0</i>

10

Table 8

Table 7. Hardwood ECF Bleaching Study			
Pulp Property at 84% Brightness			
Sequence	DEpD	D/QEpD*	D/QEpD**
ClO ₂ , %	1.9	<i>1.6</i>	<i>1.6</i>
H ₂ SO ₄ , %	0.8	<i>0</i>	<i>0</i>
NaOH, %	1.3	<i>1.1</i>	<i>1.1</i>
H ₂ O ₂ , %	0.5	<i>0.5</i>	<i>0.5</i>
DTPA, %	0	<i>0.1</i>	<i>0.1</i>
Brightness, %	84.3	<i>84.6</i>	<i>84.7</i>
Viscosity, cPs	16.8	<i>19.0</i>	<i>19.0</i>
Dirt, ppm	0	<i>0</i>	<i>0</i>
*Do/D1 ClO ₂ charge ratio = 0.8/0.8			
** Do/D1 ClO ₂ charge ratio = 1.1/0.5			

Table 7 summaries the performance results of the lab (D₀ EpD) case studies for 82% bleached pulp brightness. The expected bleached pulp brightness from the DEopD sequence would be 84%. At the same brightness, the total chemical cost reduction can be achieved by D/QEpD sequence in compared with the lab DEpD control. The viscosity of D/QEpD bleached pulp is about three points higher than that of the DEpD control pulp at the same brightness level.

Similar conclusions can be obtained for 84% bleached pulp brightness level as shown in Table 8. The viscosity of the D/QEpD pulp is 2 points higher than that of the DEpD control pulp.

Various modifications and variations may be devised given the above-described embodiments of the invention.

WHAT IS CLAIMED IS:

1. A bleaching process for bleaching a pulp having at least one Eop stage or Ep stage, the bleaching process comprising:

subjecting a brownstock pulp or oxygen delignified brownstock to a D_o/Q stage in which the pulp is first treated with chlorine dioxide in the D_o stage at a pH from about 4 to about 6 and then being treated with a chelating agent at a pH from about 4 to about 7 without interstage washing between D_o and Q stages and then being followed by a washing stage prior to treating the pulp in the Eop or Ep stage.

2. The bleaching process of claim 1 further comprising a bleaching sequence selected from the group of the formula D_o/QEop or D_o/QEp or a combination thereof wherein:

D_o is the delignification stage in which the pulp is treated at a pH from about 4 to about 6,

Q is a stage in which a pulp is treated with a chelating agent at a pH from about 4 to about 7,

Eop is an extraction stage in which pulp is treated with a composition comprising oxygen, base, and peroxide; and

Ep is an extraction stage in which pulp is treated with a composition comprising base and peroxide.

3. The bleaching process of claim 1 wherein the chelating agent is selected from the group consisting of diethylene triamine pentaacetic acid (DTPA), to aminopolycarboxylic acids (APCA), ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), phosphoric acids, ethylenediaminetetramethylene-phosphonic acid (EDTMP), diethylenetriaminepentamethylenephosphonic acid (DTPMP), nitrilotrimethylenephosphonic acid (NTMP), polycarboxylic acids, gluconates, citrates, polyacrylates, and polyaspartates or any combination of two or more thereof, or EDTA or DTPA.

4. The bleaching process of claim 1 wherein the pulp pH in the separate Q chelating stage is from about 4.5 to about 6.0.
5. The bleaching process of claim 1 wherein the pulp pH in the separate Q chelating stage is from about 5.0 to about 6.0.
6. The bleaching process of claim 1 wherein the pulp consistency in the D_o/Q stage is from about 6.0% to about 10%.
7. The bleaching process of claim 1 wherein the retention time in the separate Q stage is from about 10 min. to about 300 min.
8. The bleaching process of claim 1 wherein the temperature in the D_o/Q stage is from about 25 °C to about 120 °C.
9. The bleaching process of claim 1, wherein the temperature in the D_o/Q stage is from about 45 °C to about 50 °C
10. The bleaching process of claim 1 wherein the pulp washing stage after the D_o/Q stage removes at least about 50% of the chelated metals.
11. The bleaching process of claim 1 wherein the pulp washing stage after the D_o/Q stage removes at least about 75% of the chelated transition metals.
12. The bleaching process of claim 1 wherein the pulp washing stage after the D_o/Q stage removes substantially all of the chelated transition metals.
13. The bleaching process of claim 1 wherein an amount of hydrogen peroxide (H₂O₂) in the Eop or Ep stage is less than an amount of hydrogen peroxide (H₂O₂) used in the same or substantially the same bleaching processes without the D_o/Q stage to obtain the same or substantially the same level of pulp brightness in the Eop or Ep stage.
14. The bleaching process of claim 1 wherein the amount of AOX produced is at least about 20 % less than the amount of AOX produced in the same or substantially the same

bleaching processes without the D_o/Q stage to obtain the same or substantially the same level of pulp brightness in the Eop and/or Ep stages.

15. The bleaching process of claim 1 wherein pulp viscosity is at least about 5 % greater than the viscosity of the pulp made by the same or substantially the same bleaching processes without the D_o/Q stage.

16. The bleaching process of claim 1 wherein pulp brightness is at least about 7 % greater than the brightness of the pulp made by the same or substantially the same bleaching processes without the D_o/Q stage.

17. The bleaching process of claim 1 comprising subjecting a brownstock pulp or oxygen delignified brownstock to a D_o/Q stage in which the pulp is first treated with chlorine dioxide in the D_o stage at a pH from about 5 to about 6 without adversely affecting pulp viscosity and then being treated with a chelating agent at a pH from about 5 to about 6 without interstage washing between D_o and Q stages and then being followed by a washing stage prior to treating the pulp in the Eop or Ep stage.