

603558

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

CONVENTION APPLICATION FOR A STANDARD PATENT



We, ATOCHEM, a French Body Corporate
of La Defense 10, 4 & 8 Cours Michelet, 92800 Puteaux, France
hereby apply for the grant of a standard patent for an invention
entitled:

"PROCESS FOR BLEACHING CHEMICAL PAPER PULPS"

which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION

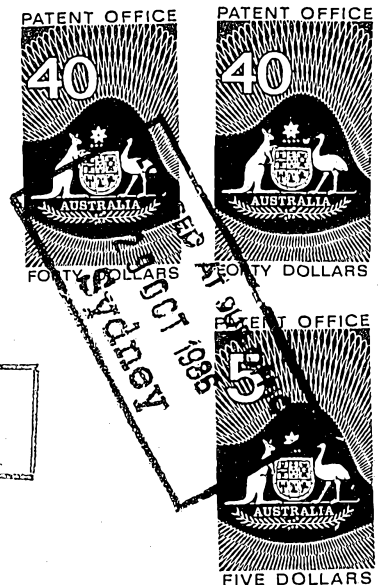
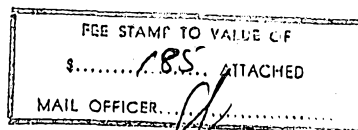
Number of Basic Application:-
85 16332

Name of Convention Country in which Basic
Application was filed:-
France

Date of Basic application:-
30 October, 1985

Our address for service is:-

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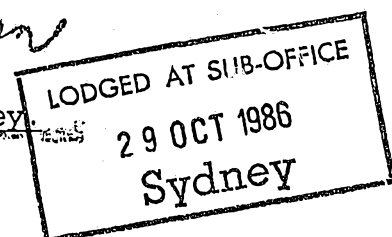
DATED this TWENTY-NINTH day of OCTOBER 1986

ATOACHEM

By:

M. J. Anderson

Registered Patent Attorney



TO: THE COMMISSIONER OF PATENTS
AUSTRALIA
SBR/JS/0080W

APPLICATION ACCEPTED AND AMENDMENTS

REMOVED 27-8-90

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-1973

DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT
OR PATENT OF ADDITION

Insert title of invention

In support of the Application made for a ~~patent~~ ^{patent of addition} for an invention
entitled:

"PROCESS FOR BLEACHING CHEMICAL PAPER PULPS"

I ~~JEAN LEBOULENGER~~
~~xxxxxx~~

care of: ATOCHEM, a French Body Corporate of:
La Defense 10, 4 & 8 Cours Michelet,
92800 PUTEAUX, France.

Insert full name(s) and address(es)
of declarant(s) being the appli-
cant(s) or person(s) authorized to
sign on behalf of an applicant
company.

Cross out whichever of paragraphs
1(a) or 1(b) does not apply
1(a) relates to application made
by individual(s)
1(b) relates to application made
by company; insert name of
applicant company.

do solemnly and sincerely declare as follows:-

1. (a) ~~I am the applicant.....for the~~ ^{patent}
~~We are~~ ^{patent of addition}
or (b) I am authorized by

ATOACHEM,

Cross out whichever of paragraphs
2(a) or 2(b) does not apply

the applicant..... for the ~~patent~~ ^{patent of addition} to make this declaration on ~~its~~ ^{their} behalf.

2. (a) ~~I am the actual inventor.....of the invention~~
~~We are~~
or (b) LUCIEN BOURSON, a citizen of France, of :

28 Avenue Gambetta, 92270 BOIS COLOMBES,
France.

2(a) relates to application made
by inventor(s)
2(b) relates to application made
by company(s) or person(s) who
are not inventor(s); insert full
name(s) and address(es) of inven-
tor(s).

~~is~~ ^{is} the actual inventor..... of the invention and the facts upon which the applicant
~~is~~ ^{is} entitled to make the application are as follows:-

state manner in which applicant(s)
derive title from inventor(s)

"The applicant would, if a patent were granted upon
an application made by the inventor, be entitled to
have the patent assigned to it".

3. The basic application..... as defined by Section 141 of the Act ~~was~~ ^{were} made

in FRANCE (NO. 8516332) on the 30TH OCTOBER 1985

by ATOCHEM.....

in on the

by

in on the

by

4. The basic application..... referred to in paragraph 3 of this Declaration ~~was~~ ^{were}
the first application..... made in a Convention country in respect of the invention ~~the~~ ^{the} subject
of the application.

Insert place and date of signature.

Declared at Puteaux this 21 day of October, 1986

Signature of declarant(s) (no
attestation required)

Jean LEBOULENGER
Jean LEBOULENGER

Note: Initial all alterations.

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PROCESS FOR BLEACHING CHEMICAL PAPER PULPS

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(55) Prior Art Documents
AU 291135 46736/64 26.1, 48.1

(57) Claim

1. A process for bleaching chemical paper pulp which comprises the following successive steps:

(a) a treatment of the pulp with a solution of chlorine and a solution of chlorine dioxide;

(b) a first alkaline extraction with a solution of sodium hydroxide in the presence of oxygen;

(c) a treatment of the pulp with a solution of chlorine dioxide;

(d) a second alkaline extraction with a solution of sodium hydroxide, said solution containing 0.5 to 2% by weight relative to the weight of the dry pulp, in the presence of 0.1 to 0.5% by weight of hydrogen peroxide relative to the weight of the dry pulp; and

(e) a further treatment of the pulp with chlorine dioxide, the total amount of chlorine dioxide used in steps (c) and (e) being at most 1% by weight relative to the weight of the dry pulp.

FORM 10

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

64492/86

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Int. Class

Complete Specification Lodged:

Accepted:

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This document contains the
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printing.

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Name of Applicant:

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Complete Specification for the invention entitled:

"PROCESS FOR BLEACHING CHEMICAL PAPER PULPS"

The following statement is a full description of this invention,
including the best method of performing it known to us

Abstract

A process for bleaching chemical paper pulp which comprises the following successive steps:

- 5 (a) a treatment of the pulp with a solution of chlorine and a solution of chlorine dioxide;
- (b) a first alkaline extraction with a solution of sodium hydroxide in the presence of oxygen;
- (c) a treatment of the pulp with a solution of chlorine dioxide;
- 10 (d) a second alkaline extraction with a solution of sodium hydroxide, said solution containing 0.5 to 2% by weight relative to the weight of the dry pulp, in the presence of 0.1 to 0.5% by weight of hydrogen peroxide relative to the weight of the dry pulp; and
- 15 (e) a further treatment of the pulp with chlorine dioxide, the total amount of chlorine dioxide used in steps (c) and (e) being at most 1% by weight relative to the weight of the dry pulp.



"PROCESS FOR BLEACHING CHEMICAL PAPER PULP"

The present invention relates to a process for bleaching chemical paper pulp.

The bleaching of chemical paper pulp, that is, unbleached cellulose pulp produced by cooking lignocellulose substances according to the so-called sulphite, sulphate or Kraft, sodium hydroxide or carbonate processes, is generally carried out in the industry by using chlorine or a chlorine derivative, which, like chlorine, is oxidizing in nature. Examples of such derivatives are chlorine dioxide (ClO_2) or sodium hypochlorite (NaOCl).

However, none of these oxidizing agents on its own is capable of ensuring a satisfactory bleaching in a single operation. It is essential to operate the bleaching process in several distinct stages and to carry out intermediate operations such as alkaline bath extraction.

The use of non-chlorinated oxidizing agents in bleaching sequences normally using chlorinated agents has been proposed in order to reduce the quantity of chlorinated agents usually employed and the disadvantages of their use, such as the production of polluting, corrosive and very strongly coloured effluents.

Thus, for example, in a bleaching sequence which typically comprises the following steps:

(a) a treatment with a solution of chlorine and chlorine dioxide;

(b) a first alkaline extraction with a solution of sodium hydroxide;

(c) a treatment with a solution of chlorine dioxide;

(d) a second alkaline extraction of the same type
5 as the first; and

(e) a second treatment with a solution of chlorine dioxide;

it has been proposed to use a reaction with oxygen during the first alkaline extraction or the reaction with hydrogen
10 peroxide during the second alkaline extraction.

The use of oxygen or the use of hydrogen peroxide in a mutually exclusive manner, makes it possible, in either case, to reduce, in a practically similar way, the amount of chlorinated bleaching agents usually required in order
15 to produce a given bleaching effect. The process is still inadequate, however, from the cost effectiveness point of view. Additionally there is not much reduction of the disadvantages mentioned above.

The process of the present invention substantially
20 overcomes the above difficulties without substantially causing any deterioration of the quality of the bleached pulp finally obtained.

Accordingly the present invention provides a chemical paper pulp bleaching sequence which successively includes a
25 treatment of the pulp with chlorine and chlorine dioxide in solution acting in a single bath, a first alkaline

extraction with sodium hydroxide in solution, a treatment of the pulp with chlorine dioxide in solution, a second alkaline extraction with a sodium hydroxide solution, said solution containing 0.5 to 2% by weight relative to the weight of the dry pulp, and a further treatment with chlorine dioxide in solution, the pulp being subjected to the action of oxygen during the first alkaline extraction and to the action of hydrogen peroxide in an amount of 0.1 to 0.5% by weight relative to the weight of the dry pulp during the second alkaline extraction, the total amount of chlorine dioxide used being at most 1% by weight relative to the weight of the dry pulp.

The process of the present invention is particularly well suited for the bleaching of softwood chemical paper pulps.

The amount of oxygen used during the first alkaline extraction is generally from 0.2% to 1% by weight relative to the weight of the dry pulp.

The treatment of the pulp with a solution of chlorine and chlorine dioxide can be carried out in a known way, preferably in a single bath, using a quantity of total active chlorine in the form of chlorine and chlorine dioxide which is generally from 3% to 10% by weight relative to the weight of the dry pulp. The quantity of chlorine dioxide advantageously represents from about 10% to 70%, preferably 10% to 50%, of the total active chlorine. The treatment may preferably be carried out at a temperature of from 20°C to 50°C, and preferably for a period of from 5 minutes to 60 minutes, the action of chlorine dioxide taking place simultaneously or, preferably, prior to that of



chlorine and the pulp having a consistency which is most commonly from approximately 3% to 5%.

The first alkaline extraction is carried out in the presence of oxygen under conditions usually employed when
5 the extraction is carried out in the absence of oxygen, at a temperature of from approximately 50°C to 80°C, for a period which is generally from 1 hour to 2 hours, with a quantity of sodium hydroxide which is generally from 2% to 5% by weight relative to the weight of the dry pulp, and
10 the consistency of the pulp preferably being from 10% to 15%.

The treatment of the pulp with chlorine dioxide, which follows the first alkaline extraction, involves a pulp having a consistency of from approximately 10% to 15%. The treatment is generally carried out for from 1 to 4
15 hours at a temperature which is generally from 60°C to 90°C.

The second alkaline extraction, carried out in the presence of hydrogen peroxide, is generally performed at a temperature of from approximately 70°C to 90°C, preferably for from 0.5 to 2 hours, using a quantity of sodium
20 hydroxide which ~~generally~~ represents from 0.5% to 2% by weight relative to the weight of the dry pulp. The consistency of the pulp is generally from 10% to 15%.

The treatment of the pulp with chlorine dioxide, which follows the second alkaline extraction, is usually
25 carried out under conditions analogous to those described for the treatment with the same reagent which follows the first alkaline extraction.



The total quantity of chlorine dioxide used in the two treatments of the pulp with this reagent depends on the conditions chosen for the combined use of oxygen and of hydrogen peroxide. The quantity is generally much
5 lower than the 1% to 4% by weight relative to the weight of the dry pulp, which is usually required, in the absence of the combined use of oxygen and hydrogen peroxide according to the invention, to achieve the same bleaching effect as that obtained when operating according to the
10 invention.

In the present invention, the total quantity of chlorine dioxide used ^{is} preferably ~~does not exceed 1%, and more preferably is~~ less than 0.5%, by weight relative to the weight of the dry pulp.

15 The Examples below either illustrate the invention or are given by way of comparison.

The following symbols have been used for denoting the different successive stages in the bleaching sequence:

C/D: treatment of the pulp with chlorine dioxide
20 and with chlorine in a single bath, the action of chlorine dioxide preceding that of chlorine.

E₁: alkaline extraction with a solution of sodium hydroxide.

E₁/O: E₁ alkaline extraction with a solution of
25 sodium hydroxide in the presence of oxygen.

D₁: treatment of the pulp with chlorine dioxide,



which follows either E_1 or E_1/O .

E_2 : same meaning as E_1 .

E_2/P : E_2 alkaline extraction with a solution of sodium hydroxide in the presence of hydrogen peroxide.

5 D_2 : same meaning as D_1 , D_2 being carried out after either E_2 or E_2/P .

In all Examples, the quantities of reagents are expressed in percent by weight relative to the weight of dry pulp, except where indicated otherwise.

10 The condition of the pulp is defined by its degree of polymerization (dp) and by its whiteness expressed in degrees ELREPHO ($^{\circ}ER$) as can commonly be determined by a person skilled in the art by means of an ELREPHO spectrophometer made by CARL ZEISS.

15 EXAMPLE 1

An unbleached softwood KRAFT pulp having a KAPPA index, which is a measure of the lignin content of the pulp, of 30 and a whiteness of $26.6^{\circ}ER$, is subjected to C/D under the following conditions:

20 total active chlorine: 5.7%

active chlorine from ClO_2 : 14% of the total active chlorine.

action of ClO_2 : temperature : $25^{\circ}C$

period : 0.25 hour

25 action of Cl_2 : temperature : $40^{\circ}C$

period : 0.5 hour

pulp, consistency: 3.2%

The alkaline extraction $E_1/0$ which follows is carried out under the following conditions:

NaOH: 3.9%

5 O_2 : 0.5%

temperature: 60°C, (the pressure being 2 bar (2×10^5 Pa))

period: 1.5 hours

pulp, consistency: 10%

D_1 is then carried out as follows:

10 ClO_2 : 0.3%

temperature: 70°C

period: 2.5 hours

pulp, consistency: 10%,

E_2/P as follows:

15 NaOH : 0.75%

H_2O_2 : 0.20%

temperature: 80°C

period 1.5 hours

pulp, consistency: 10%,

20 and finally, D_2 in the following way:

ClO_2 : 0.2%

temperature: 80°C

period: 2.5 hours

pulp, consistency: 10%

The bleached pulp which finally results from this bleaching sequence has a whiteness of 90.1° ER.

For the purpose of comparison, the same sequence is carried out omitting the use of oxygen and hydrogen peroxide.

5 A whiteness of 88.4° ER is obtained only when, in comparison with the process according to the invention, a quantity of ClO_2 which is 4 times greater during D_1 and 3 times greater during D_2 is employed.

Again for the purpose of comparison, when, compared
10 with the process of the invention, the use of either oxygen or hydrogen peroxide is omitted, a whiteness of 89° ER is obtained when at least twice as much ClO_2 is used during D_1 and D_2 than is required when operating according to the invention.

15 Finally, the use of the same quantities of ClO_2 in D_1 and in D_2 as is used in the process of the present invention leads to a much lower whiteness of the pulp obtained when the oxygen and hydrogen peroxide treatments are omitted.

Thus, if the quantities of ClO_2 mentioned in the
20 process of the invention described at the beginning of this Example are used in D_1 and D_2 , but the use of hydrogen peroxide is omitted, the whiteness of the pulp finally obtained is only 84.9° ER.

The process carried out according to the invention
25 gives a bleached pulp the characteristics of which, especially the d_p , are at least equal to those of bleached pulps obtained by known processes, in spite of the fact

that the opposite could perhaps have been expected.

EXAMPLE 2

The process of Example 1 is carried out until D_1 , but, from D_1 onwards, in a way which differs from that of Example 1 in that the quantities of ClO_2 employed in D_1 and D_2 are 0.1% and 0.4% respectively and in that the quantity of hydrogen peroxide in E_2/P is only 0.1%. The whiteness of the pulp thereby bleached is nearly 88.5° ER.

This Example illustrates the fact that even when only a very small quantity of hydrogen peroxide is employed, the enhancing effect of the combined actions of oxygen and hydrogen peroxide according to the invention is retained.

The claims defining the invention are as follows:

1. A process for bleaching chemical paper pulp which comprises the following successive steps:

(a) a treatment of the pulp with a solution of chlorine and a solution of chlorine dioxide;

(b) a first alkaline extraction with a solution of sodium hydroxide in the presence of oxygen;

(c) a treatment of the pulp with a solution of chlorine dioxide;

(d) a second alkaline extraction with a solution of sodium hydroxide, said solution containing 0.5 to 2% by weight relative to the weight of the dry pulp, in the presence of 0.1 to 0.5% by weight of hydrogen peroxide relative to the weight of the dry pulp; and

(e) a further treatment of the pulp with chlorine dioxide, the total amount of chlorine dioxide used in steps (c) and (e) being at most 1% by weight relative to the weight of the dry pulp.

2. A process according to claim 1, wherein the pulp is a softwood pulp.

3. A process according to claim 1 or 2, wherein the quantity of oxygen employed in step (b) is from 0.2% to 1% by weight relative to the weight of the dry pulp.

4. A process according to any one of claims 1 to 3, wherein step (b) is carried out at a temperature of from 50°C to 80°C using from 2% to 5% sodium hydroxide by weight relative to the weight of the dry pulp.

5. A process according to any one of claims 1 to 4, wherein the consistency of the pulp in step (b) is from 10% to 15%.

6. A process according to any one of claims 1 to 5 wherein step (d) is carried out at a temperature of from 70°C to 90°C using from 0.5% to 2% sodium hydroxide by weight relative to the weight of the dry pulp.

7. A process according to any one of claims 1 to 6, wherein the consistency of the pulp during step (d) is from 10% to 15%.

8. A process according to any one of claims 1 to 7, wherein the treatment of the pulp in step (a) is carried out at a temperature of from 20°C to 50°C, the quantity of total active chlorine in the form of chlorine and of chlorine dioxide being from 3% to 10% by weight relative to the weight of the dry pulp.

9. A process according to claim 8, wherein the chlorine dioxide represents 10% to 70% of the total active chlorine.



10. A process according to claim 9 wherein the chlorine dioxide represents 10% to 50% of the total active chlorine.

11. A process according to any one of claims 1 to 10 wherein the consistency of the pulp in step (a) is from 3% to 5%.

12. A process according to any one of claims 1 to 11 wherein in step (a) the pulp is first treated with chlorine dioxide and subsequently treated with chlorine.

13. A process according to any one of claims 1 to 12 wherein steps (c) and (e) are each carried out at a temperature of from 60°C to 90°C.

14. A process according to any one of claims 1 to 13 wherein the treatment with chlorine dioxide in steps (c) and (e) involves a pulp having a consistency of from 10% to 15%.

15. A process according to any one of claims 1 to 14 wherein the total amount of chlorine dioxide used in steps (c) and (e) totals at most 0.5% by weight relative to the weight of the dry pulp.

16. A process according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

17. A bleached chemical paper pulp when produced by a process according to any one of the preceding claims.

DATED this TWENTY-SECOND day of AUGUST 1990

Atochem

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

