(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 395 792 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication of patent specification: **14.07.93**

(51) Int. Cl.[5]: **D21C 9/10**, D21C 9/147

(21) Application number: **89117233.0**

(22) Date of filing: **18.09.89**

(54) **Procedure for the bleaching of pulp.**

(30) Priority: **04.05.89 FI 892151**

(43) Date of publication of application:
07.11.90 Bulletin 90/45

(45) Publication of the grant of the patent:
14.07.93 Bulletin 93/28

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI NL SE

(56) References cited:
EP-A- 0 383 999
WO-A-89/08738

STFI/SPCI, THIRD INTERNATIONAL CONFERENCE BIOTECHNOLOGY IN THE PULP & PAPER INDUSTRY, Stockholm (SE), 16-19 June 1986; L. VIIKARI et al., pp. 67-69*

ABSTRACTS BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 59, no. 4, October 1988, Appleton (US); A. KANTELINEN et al., p. 431, no. 4037*

(73) Proprietor: **ENSO-GUTZEIT OY**
Kanavaranta 1
SF-00160 Helsinki(FI)

(72) Inventor: **Vaheri, Marja**
Lystimäenkuja 1 A
SF-02210 Espoo(FI)
Inventor: **Miikki, Kari**
Hilkankatu 10
SF-55100 Imatra(FI)
Inventor: **Jokela, Veikko**
Rantatie
SF-55330 Tiuruniemi(FI)
Inventor: **Ruohoniemi, Kimmo**
Harakantie 586 as
SF-55800 Imatra(FI)

(74) Representative: **Weitzel, Wolfgang, Dr.-Ing.**
Friedenstrasse 10
W-7920 Heidenheim (DE)

EP 0 395 792 B1

Description

The present invention relates to a procedure for the bleaching of pulp, in which procedure the oxidating bleaching chemical is oxygen. Reference is made to EP-A-0 383 999.

Especially pulp obtained from a sulphate pulping process is of brown colour, which is mainly due to the lignin remaining in the pulp. Lignin is removed from the pulp by bleaching, which is a process consisting of several stages. During this process, the pulp is treated alternately with oxidizing, lignin-degrading chemicals and chemicals dissolving the degradation products. Oxidizing agents commonly used are oxygen and chlorine-containing chemicals, whereas alkali solutions are used for eliminating the degradation products.

In the reactions occurring in bleaching using chemicals containing chlorine, lignin is converted into organic chlorine compounds, which remain in the spent bleach liquor removed from the pulp. Spent bleach liquors are a problem in regard of environmental protection because of the toxic nature of the chlorophenols and other possible organic chlorine compounds contained in the liquors. Besides, the chemical oxygen demand in spent bleach liquors reaches detrimental levels. As the measures aimed at reducing the environmental pollution load resulting from sulphate pulp production have so far been mainly concentrated on other parts of the process except bleaching, the relative significance of bleaching as a polluting factor has been increasing.

The spent bleach liquors causing the worst environmental pollution load are produced during the washing following the first chlorination and the first alkali treatment in the bleaching process. Various methods have been employed to reduce the pollution load, e.g. by replacing chlorine gas with chlorine dioxide or using oxygen as the oxidizing agent in the first bleaching stage, or by biological purification of the spent bleach liquor. However, the results achieved by these methods have not been completely satisfactory. Although the amounts of chlorophenols and other toxic chlorine compounds in the spent bleach liquor have been significantly reduced by employing chlorine dioxide and oxygen bleaching, it has not been possible to achieve a sufficient reduction in the chemical oxygen demand values of the liquors. Therefore, the methods referred to have required the employment of efficient biological purification.

The above identified document EP-A-0 383 999 has an earlier priority date than this application, however, was published later. The same is true for WO-A-8 908 738. This document is directed towards the effect of the enzyme treatment on the reduction of the chlorine content of bleached pulp. As is mentioned therein, chlorine chemicals are used in the bleach, whereby the proportion of chlorine dioxide is small.

Int. Cont. Biotechnol. Pulp & Paper Ind. (1986), 67-69, discloses a bleaching process, wherein the proportion of gaseous chlorine was high. However, this document does not teach the use of enzymes as a means for the reduction of the chlorine content in waste waters.

The object of the present invention is to achieve a solution that enables the toxic content and the value of chemical oxygen demand of the spent bleach liquor to be reduced so as to reduce the need for purification of the liquor. The invention is based on oxygen bleaching and it is characterized in that oxygen is used in the first oxidation stage of the bleaching process, that the pulp is subjected to enzyme treatment, and that after the oxygen bleaching and enzyme treatment, the pulp is washed.

It has been observed in earlier investigations that by using enzymes it is possible to separate lignin and/or hemicellulose from cellulose and thus give the pulp a more spongy quality. This justifies the assumption that if the pulp obtained from the digestion process is first subjected to enzyme treatment, it is possible to reduce the amount of chemicals needed in the next bleaching stage. According to the invention, it has now been observed that enzyme treatment involves an essential reduction in the amount of toxic compounds in the spent bleach liquor while at the same time reducing its chemical oxygen demand, especially when the oxidizing chemical used in the first bleaching stage is oxygen. When the commonest oxidizing chemical, i.e. pure chlorine gas, is used, enzyme treatment has a substantially weaker effect on the quality of the spent bleach liquor.

According to the invention, the pulp can be subjected to enzyme treatment and washing before the first oxidation stage. A preferable alternative solution is to carry out the enzyme treatment and washing after the first oxidation stage. The enzyme breaks down hemicellulose and/or lignin contained in the pulp and renders the pulp more spongy, thus enhancing the effect of the chemicals in subsequent oxidation and alkali treatment stages. By washing the pulp after the enzyme treatment, the degradation products are removed and can be directed to incineration so that they will not contribute to the pollution load at all but are instead utilized in the energy handling system of the plant.

According to the invention, the subsequent oxidation stages after oxygen bleaching can be implemented using a bleaching chemical containing chlorine, e.g. chlorine gas and/or chlorine dioxide. The production of detrimental chlorine compounds will thus be limited to these process stages, and to minimize the amounts of these compounds it is preferable to use chlorine dioxide to as large an extent as possible.

This makes it possible to reduce the content of organic chlorine compounds in the spent bleach liquor by more than 70% even in the bleaching of softwood pulp. This is a result unattainable with previously known bleaching methods.

Except for the enzyme treatment, the bleaching of pulp by the procedure of the invention can be performed by employing alternate oxidation and alkali phases and washing the pulp after each of these phases to remove the bleaching chemicals and degradation products.

The enzyme treatment in the procedure of the invention is preferably carried out in a temperature range of 10-90 °C, the most suitable range being 40-80 °C, with pH values in the range 3.0-10.0, most suitably 4.0-8.0. The enzyme used can be a hemicellulase, cellulase, pectinase, esterase or a mixture of these.

In the following, the invention is described in greater detail by the aid of embodiment examples based on laboratory experiments.

Example 1

A diluted enzyme mixture KD 50 (hemicellulase) was added to 220 g of dry matter obtained from pine sulphate pulp (with a dry matter content of 30%) so that a mixture with a consistency of 10% and a xylanase activity of 5 U/g of pulp dry matter was obtained. The temperature in the enzyme treatment was 55 °C and the duration of treatment 2 h.

After the enzyme treatment the pulp was subjected to preliminary oxygen bleaching. The acidity of the pulp was adjusted to pH 12. In the oxygen treatment the temperature was 100 °C, overpressure 2 bar and duration of treatment 45 min. After oxygen treatment the pulp was washed in a Buchner funnel with a 20-fold amount of water.

Next, the pulp was subjected to an oxidizing bleaching treatment using a mixture containing 50 % chlorine dioxide and 50 % chlorine gas. Of this mixture, a dose equal to 2.0 x kappa number after oxygen bleaching was used. Treatment temperature was 40 °C and duration 45 min. After oxidation the pulp was washed in a Buchner funnel with a 20-fold amount of water.

Next, the mass was subjected to an alkali treatment using a 5 % sodium hydroxide solution in a dose of 0.9 x kappa. Consistency of solution was 10 %, treatment temperature 60 °C and duration of treatment 90 min. After the alkali treatment the pulp was washed in the same way as after oxidation.

After this, the bleaching was continued by repeating the oxidation and alkali phases and then once more the oxidation phase and washing the pulp between these phases as described above. With these arrangements, the amount of chlorine dioxide in the second oxidation phase was 26 % and in the third phase 13 % of the amount of chlorine dioxide in the first oxidation phase. In both cases the dosage of sodium hydroxide was 1 % of the amount of chemical pulp.

The amounts of bleaching chemicals consumed and the analysis results describing the quality of the bleached pulp are presented in Table 1 (experiment 3).

In addition to the above-described experiment (exp. 3) illustrating the invention, two reference experiments (experiments 1 and 2) and an additional experiment (exp. 4) were carried out, and the results obtained from these are also presented in Table 1 below. The experiments were performed as follows:

Experiment 1 (reference): No enzyme treatment and no preliminary oxygen bleaching were employed. The dosage of chlorine chemicals, of which 90 % consisted of chlorine gas and 10 % of chlorine dioxide, was such that the same target bleaching degree of 89.0 was reached as in experiments 3 and 4. Otherwise the experiment was analogous to that described above (exp. 3).

Experiment 2 (reference): No enzyme treatment was employed. In other respects the experiment was analogous to that described above.

Experiment 4: The pulp was first subjected to preliminary oxygen bleaching and washing and then enzyme treatment. Each phase was performed in the manner described above (exp. 3), only the order of the treatments was reversed. In other respects the experiment was analogous to that described above (exp. 3). The present invention comprises a procedure employing the principle of this experiment.

TABLE 1

	C/D(90/10)-E-DED Exp. 1	O-D/C(50/50)-E-DED Exp. 2	Enz-O-D/C(50/50)-E-DED Exp. 3	O-enz-D/C(50/50)-E-DED Exp. 4
CONSUMPTION OF ACTIVE chlorine kg/t of chem. pulp	100	64	54	51
- chlorine gas kg/t of chem. pulp	63	14.6	13.7	12.6
- ClO_2 kg/t of chem. pulp	13.2	18.9	15.4	14.7
Amount of equivalents of chlorine	70	24	21.4	19.9
Saving in equivalents of chlorine %	0	66	70	72
Chlorine (%) saved due to enzyme		0	11	17

The results indicate that the amount of chlorine in the bleaching process can be substantially reduced by subjecting the pulp as taught by the invention to preliminary oxygen bleaching and enzyme treatment and replacing part of the chlorine gas, conventionally used in bleaching, with chlorine dioxide. It is worth noting that oxygen bleaching and the use of chlorine dioxide in themselves represent known technology and that the delignifying effect of enzymes is known from certain scientific publications, but that the use of a combination of these as taught by the invention, leading to particularly favourable results, has not been known until now.

Furthermore, it is to be noted that, in the bleaching procedure of the invention, the liquids obtained from the washing stages phases after oxidation and enzyme treatment can be burned in a soda recovery boiler, in which case the amount of organic matter left in the spent bleach liquor is substantially smaller than in conventional chlorine bleaching and also smaller than in oxygen bleaching carried out without using an enzyme.

Example 2

Preliminary oxygen bleaching of 670 g of brown pine sulphate pulp (dry matter content 30 %) was performed as follows: The pH value of the pulp was adjusted to 12 using NaOH, whereupon the pulp was subjected to a 45-min. oxygen treatment in an autoclave at a temperature of 100 °C and an oxygen overpressure of 2 bar.

After oxidation the pulp was washed in a Buchner funnel with a 20-fold amount of water.

Next, the pulp was acidated with sulphuric acid to pH 6. An amount of diluted enzyme mixture (Trichoderma [r] hemicellulase MK 901, Cultor Oy) was then added to the pulp so that a mixture consistency of 10 % and xylanase activity of 5 U/g of pulp dry matter was obtained. The pulp was subjected to a 2-hour enzyme treatment at 55 °C.

After the enzyme treatment the pulp was washed using NaOH in a dosage of 1.5 % of pulp dry matter. Consistency in the alkali phase was 10 %, duration of treatment 90 min. and temperature 60 °C. After the alkali treatment the pulp was washed in a Buchner funnel with a 20-fold amount of water.

Next, the pulp was subjected to an oxidating bleaching treatment using chlorine dioxide in a dosage of 6.6 % of pulp dry matter. Consistency of the mixture was 10 %, temperature during treatment 70 °C, and duration of treatment 180 min. After the treatment the pulp was washed in a Buchner funnel with a 20-fold amount of water.

Next, the pulp was treated with NaOH (amount of NaOH 1 % of the dry matter of the pulp) for 90 min. Viscosity of the pulp was 10 %. After treatment, the pulp was washed with a 20-fold amount of water.

As the last bleaching stage, the pulp was subjected to a chlorine dioxide treatment. The dosage of chlorine dioxide was 3.3 % of pulp dry matter, mixture viscosity 10 %, treatment temperature 75 °C and duration 240 min. After treatment, the pulp was again washed with a 20-fold amount of water.

All of the wash water was collected and analyzed to determine the quantities of organic chlorine compounds (AOX) and the chemical oxygen demand (COD) of the water. The results are presented in Table 2.

In addition to the above-described experiment (exp. 3) illustrating the invention, two reference experiments (exp. 1 and exp. 2) and two further experiments (experiments 4 and 5) illustrating the invention were carried out. The results of all these experiments are also presented in Table 2 below.

Experiment 1 (reference): No enzyme treatment and no preliminary oxygen bleaching of the pulp were employed. The dosage of chlorine chemicals, of which 90 % consisted of chlorine gas and 10 % of chlorine dioxide while in the other bleaching stages the proportion of chlorine dioxide was 100 %, was such that the same target degree 87 of bleaching was reached as in experiments 2,3,4 and 5.

Experiment 2 (reference): Instead of an enzyme treatment, the pulp was subjected to normal preliminary oxygen bleaching and chlorine/chlorine dioxide (80/20) treatment. The preliminary oxygen bleaching was performed as in experiment 3 and the dosage of chlorine chemicals was such that the target bleaching degree of 87 was achieved.

Experiment 4: The pulp was subjected to preliminary oxygen bleaching, enzyme treatment and chlorine dioxide bleaching as in example 3, but in the alkali washing stage oxygen was supplied so that a 2-bar oxygen overpressure prevailed in the reaction vessel.

Experiment 5: The pulp was treated as in experiment 4 except for the first chlorine chemical treatment phase, in which the chlorine chemical was 80 % chlorine dioxide and 20 % chlorine gas. The dosage of active chlorine was 2.3 x kappa. In the next chlorine dioxide treatment phase the chemical was 100 % chlorine dioxide, and the dosage was 2.9 %.

TABLE 2

	C/D(90/10)-E-DED Exp. 1	O-C/D(80/20)-E-DED Exp. 2	O-Enz-E-DED Exp. 3	O-Enz-OE-DED Exp. 4	O-Enz-OE-D/C(80/20)ED Exp. 5
CONSUMPTION OF ACTIVE chlorine kg/t of chem. pulp	100	73	95	87	62
- chlorine gas kg/t of chem. pulp	63	30	-	-	10
- ClO_2 kg/t of chem. pulp	13	16	37	34	20
AMOUNT OF EQUIVALENTS OF CHLORINE	78	38	19	17	20
AOX (kg/t)	4.0	2.5	1.8	1.6	1.0
Reduction in AOX (%)	0	38	55	60	75
COD (kg/t)	71	40	35	35	35
Reduction in COD (%)	0	44	51	51	51

As can be seen by the results presented in Table 2, the amount of organic chlorine compounds in the spent bleach liquor produced in the bleaching of pine sulphate pulp is reduced to the level of 1.8 kg per ton of chemical pulp when oxygen bleaching and enzyme treatment are combined. The same degree of bleaching is achieved by both methods.

The results indicate that the amount of chlorine in the bleaching process can be substantially reduced if the pulp is treated as provided by the invention by subjecting it to preliminary oxygen bleaching, enzyme treatment and oxygen alkali washing after the enzyme treatment and replacing all or most of the conventionally used chlorine gas with chlorine dioxide. Such a procedure allows the amount of organing chlorine compounds in the spent bleach liquor to be substantially reduced, even by more than 70 %. If the spent bleach liquors from all those stages which precede bleaching stages involving chlorine chemicals are subjected to burning, then the chemical oxygen demand of the spent bleach liquor will also be reduced by more than 50 %.

It is obvious to a person skilled in the art that different embodiments of the invention are not restricted to the examples described above, but that they may instead be varied within the scope of the following claims.

Claims

1. Procedure for the bleaching of pulp, in which procedure as the oxidating bleaching chemical is oxygen, **characterized** in that oxygen is used in the first oxidation stage of the bleaching process, that the pulp is subjected to enzyme treatment, and that after oxygen bleaching and enzyme treatment, the pulp is washed.

2. Procedure according to claim 1, **characterized** in that the enzyme treatment takes place before the first oxidation stage.

3. Procedure according to claim 1, **characterized** in that the enzyme treatment takes place after the first oxidation stage.

4. Procedure according to any one of the preceding claims, **characterized** in that the subsequent oxidation stages of the bleaching process are implemented using a bleaching chemical containing chlorine, e.g. chlorine gas and/or chlorine dioxide.

5. Procedure according to claim 4, **characterized** in that, between said subsequent oxidation stages, the pulp is treated with an alkali, such as sodium hydroxide.

6. Procedure according to any one of the preceding claims, **characterized** in that the enzyme used is a hemicellulase, cellulase, pectinase, esterase or a mixture of these.

7. Procedure according to any one of the preceding claims, **characterized** in that the enzyme treatment is carried out in a temperature range of 10-90 °C, preferably 40-80 °C, with pH values in the range 3.0-10.0, preferably 4.0-8.0.

8. Procedure according to any one of the preceding claims, **characterized** in that the procedure is applied in the bleaching of softwood pulp.

Patentansprüche

1. Verfahren zum Bleichen von Zellstoff, wobei die oxydiedierende Bleichchemikalie Sauerstoff ist, dadurch gekennzeichnet, daß der Sauerstoff in der ersten Oxydationsstufe des Bleichprozesses angewandt wird, daß der Zellstoff einer Enzymbehandlung unterworfen wird, und daß der Zellstoff nach der Sauerstoffbleiche und der Enzymbehandlung gewaschen wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Enzymbehandlung vor der ersten Oxydationsstufe stattfindet.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Enzymbehandlung nach der ersten Oxydationsstufe stattfindet.

4. Verfahren nach einem der vorausgehenden Ansprüche, dadurch gekennzeichnet, daß die nachfolgenden Sauerstoffstufen des Bleichverfahrens verwirklicht werden durch Anwendung einer Bleichchemikalie, die Chlor enthält, z.B. Chlorgas und/oder Chlordioxyd.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß zwischen den genannten aufeinander folgenden Oxydationsstufen der Zellstoff mit Alkali wie Natriumhydroxid behandelt wird.

6. Verfahren nach einem der vorausgegangenen Ansprüche, dadurch gekennzeichnet, daß das verwendete Enzym eine Hemizellulase, eine Zellulase, eine Pektinase, eine Esterase oder ein Gemisch aus diesen ist.

7. Verfahren nach einem der vorausgegangenen Ansprüche, dadurch gekennzeichnet, daß die Enzymbehandlung bei einem Temperaturbereich von 10-90 °C, am besten 40-80 °C, und bei pH-Werten im Bereich von 3,0-10,0, am besten 4,0-8,0 durchgeführt wird.

8. Verfahren nach einem der vorausgegangenen Ansprüche, dadurch gekennzeichnet, daß das Verfahren beim Bleichen von Nadelholzzellstoff angewandt wird.

Revendications

1. Procédé de blanchiment de pâte, dans lequel le produit chimique de blanchiment oxydant est de l'oxygène, procédé caractérisé en ce que l'oxygène est utilisé dans la première étape d'oxydation du processus de blanchiment, en ce que la pâte est soumise à un traitement par une enzyme, et en ce qu'on lave la pâte après le blanchiment à l'oxygène et le traitement à l'enzyme.

2. Procédé selon la revendication 1, caractérisé en ce que le traitement à l'enzyme est effectué avant la première étape d'oxydation.

3. Procédé selon la revendication 1, caractérisé en ce que le traitement à l'enzyme est effectué après la première étape d'oxydation.

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que les étapes d'oxydation ultérieures du processus de blanchiment sont effectuées en utilisant un produit chimique de blanchiment contenant du chlore, comme par exemple du chlore gazeux et/ou du dioxyde de chlore.

5. Procédé selon la revendication 4, caractérisé en ce que, entre les étapes d'oxydation ultérieures, la pâte est traitée par un produit alcalin tel que de l'hydroxyde de sodium.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'enzyme utilisée est une hémicellulase, une cellulase, une pectinase, une estérase ou un mélange de ces produits.

7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le traitement à l'enzyme est effectué dans une plage de températures de 10° à 90 °C, et de préférence de 40° à 80 °C, avec des valeurs de pH se situant dans la plage de 3,0 à 10,0 et de préférence de 4,0 à 8,0.

8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ce procédé est appliqué au blanchiment de pulpe de bois tendre.