

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 408 803 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **89117234.8**

(51) Int. Cl.⁵: **D21C 9/10, D21C 9/14**

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

(30) Priority: **10.07.89 FI 893338**

(43) Date of publication of application:
23.01.91 Bulletin 91/04

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

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

(57) The invention concerns a procedure for the bleaching of pulp, in which procedure an oxidating bleaching chemical containing chlorine is used. The essential feature of the invention is that the pulp is treated, either in conjunction with or before oxidation, with a lignin-modifying oxidation-reduction enzyme, such as the lactase produced by the white-rot fungus. The oxidating bleaching chemical used in the procedure may be chlorine dioxide or a mixture of chlorine dioxide and chlorine gas. The use of said enzyme reduces the amount of chlorophenols and other forms of organically bound chlorine in the spent bleach liquor, simultaneously lowering its chemical oxygen demand.

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PROCEDURE FOR THE BLEACHING OF PULP

The present invention relates to a procedure for the bleaching of pulp, in which procedure an oxidating bleaching chemical containing chlorine is used.

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 generally 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 chlorine-containing chemicals and oxygen, whereas alkali solutions are used for eliminating the degradation products.

In the reactions occurring in bleaching using chlorine-containing chemicals, lignin is converted into organic chlorine compounds, which remain in the spent bleach liquor. Spent bleach liquors are a problem in regard of environmental protection because of the possible toxic nature of the organic chlorine compounds contained in the liquors. Moreover, the chemical oxygen demand in spent bleach liquors reaches detrimental levels.

The spent bleach liquors causing the worst environmental pollution load are produced in the washing stages following the first chlorination and the first alkali treatment in the bleaching process. To reduce the pollution load, various methods have been employed, including the use of chlorine dioxide instead of chlorine gas, the use of oxygen as an oxidating chemical in the first bleaching stage, and biological purification of the spent bleach liquor. However, these methods have not yielded completely satisfactory results. Although the amounts of chlorophenols and other toxic chlorine compounds in the spent bleach liquor have been significantly reduced by using chlorine dioxide and employing oxygen bleaching, it has not been possible to achieve a sufficient reduction in the chemical oxygen demand values of the effluents. Therefore, the methods referred to have required the employment of efficient biological purification.

The object of the present invention is to achieve a pulp bleaching procedure that enables the toxic content and 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 characterized in that, in conjunction with or before oxidation, the pulp is subjected to an enzyme treatment using an oxidation-reduction enzyme modifying lignin.

It has been observed in earlier investigations that by using enzymes degrading hemicellulose it is possible to separate lignin and/or hemicellulose from cellulose and thus make the pulp more easily bleachable in the subsequent bleaching stages. This effect has not been observed before in conjunction with the use of lignin-degrading enzymes.

According to the invention, it has now been observed that a treatment with a suitable redox enzyme reduces the amount of chlorine chemicals required for bleaching, thereby also reducing the amounts of organic chlorine compounds left in the spent bleach liquor.

According to the invention, the redox potential of the enzymatic reaction should be below 400 mV, preferably below 250 mV. Suitable redox enzymes are e.g. phenoloxidases, such as the lactase produced by the white-rot fungus.

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

The enzyme treatment as taught by 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, preferably 4.0-8.0. The enzyme used is a lignin-modifying oxidation-reduction enzyme, e.g. a lactase as mentioned above.

The invention also concerns the use of a lignin-modifying enzyme, e.g. the lactase produced by the white-rot fungus, in the bleaching of pulp using an oxidating bleaching chemical containing chlorine.

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

Example 1

A diluted enzyme mixture of lactase produced by the *Trametes hirsuta* white-rot fungus 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 lactase activity of 60 U/kg 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 filtered in a Buchner funnel and the pulp cake obtained was washed with ion-

exchange-treated water so that a wash ratio of 20 was obtained.

For reference, a corresponding portion of pulp was treated in the same way except that no enzyme was added.

Next, both the pulp quantity which had undergone enzyme treatment and the reference portion were
5 bleached by a process consisting of five successive stages of oxidation and leaching. In the first stage, the
chemicals used were chlorine (90%) and chlorine dioxide (10%), in the second stage sodium hydroxide, in
the third stage chlorine dioxide, in the fourth stage sodium hydroxide and in the fifth stage chlorine dioxide.

The consumption of bleaching chemicals and the analysis results representing the quality of the
bleached pulp are presented in Table 1.

10 The experiment shows that by using a lignin-modifying enzyme, i.e. lactase, a substantial reduction in
the amount of chlorine has been achieved.

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TABLE 1

5	Enzyme treatment, pine sulphate pulp, kappa 27.4	Final pH	Viscosity	Kappa	Yield%
	Reference portion	8.70	1020	26.4	100.84
	Enzyme-treated pulp	8.60	1045	26.5	100.63
10	Experiment continues with bleaching sequence D/C-E-D-E-D				
	Phase D/C 10/90	Reference		Enzyme-treated	
	D/C 2* kappa			pulp	
	D/C dosage %	5.28		5.30	
	consumption %	5.28		5.30	
15	pH	1.65		1.55	
	consistency	3.5		3.5	
	temperature °C	55		55	
	duration min.	45		45	
20	Phase E				
	E 0.9*kappa				
	E dosage %	2.38		2.39	
	pH	11.65		11.3	
	kappa	9.6		8.2	
	yield %	96.13		96.81	
25	Phase D				
	dosage %	3.0		3.0	
	consumption %	3.0		3.0	
	pH	1.9		1.8	
	consistency %	10		10	
	temperature °C	70		70	
30	duration min.	180		180	
	Phase E2				
	dosage %	1.0		1.0	
	pH	11.2		11.3	
	consistency %	10		10	
35	temperature °C	60		60	
	duration min.	90		90	
	Phase D2				
	dosage %	1.0		1.5	
	consumption %	1.5		1.42	
40	pH	2.2		2.2	
	consistency %	10		10	
	temperature °C	75		75	
	duration min.	240		240	
	acidation pH	4.2		3	
	yield %	97.96		98.18	
45	total yield %	94.96		95.65	
	degree of bleaching	83.8		87.1	
	viscosity				
	TCl mg/kg	345		265	
50	DKM extract %				

Claims

- 55 1. Procedure for the bleaching of pulp, said procedure using an oxidating bleaching chemical containing chlorine, **characterized** in that, in connection with or before oxidation, the pulp is subjected to an enzyme treatment in which a lignin-modifying oxidation-reduction enzyme is used.
2. Procedure according to claim 1, **characterized** in that the redox potential of the enzymatic reaction is

below 400 mV, preferably below 250 mV.

3. Procedure according to claim 1 or 2, **characterized** in that the enzyme used is a lignin-modifying phenoloxidase, such as the lactase produced by the white-rot fungus.

4. Procedure according to any one of the preceding claims, **characterized** in that the pulp is treated with a phenoloxidase, e.g. lactase, and washed before the first oxidation phase.

5. Procedure according to any one of the preceding claims, **characterized** in that the bleaching chemical used in the oxidation phases is chlorine dioxide or a mixture of chlorine dioxide and chlorine gas, and that between the oxidation phases the pulp is treated with an alkali.

6. 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.

7. Procedure according to any one of the preceding claims, **characterized** in that the procedure is used for the bleaching of softwood pulp, e.g. pine sulphate pulp.

8. Use of a lignin-modifying oxidation-reduction enzyme in a pulp bleaching process using an oxidating bleaching chemical containing chlorine.

9. Use of a phenoloxidase, e.g. the lactase produced by the white-rot fungus, in a pulp bleaching process using an oxidating bleaching chemical containing chlorine.

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EUROPEAN SEARCH REPORT

Application Number

EP 89 11 7234

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-3 636 208 (H.-P. CALL) * The whole document * - - -	1,5-7	D 21 C 9/10 D 21 C 9/14
A	TAPPI, vol. 67, no. 10, October 1984, pages 31-33; R. FARRELL: "Biocatalysts hold promise of better pulp quality" * The whole document * - - - - -	1,3,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 21 C
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		29 October 90	BERNARDO NORIEGA F.
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