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(54) **A PROCESS FOR THE BLEACHING OF CHEMICAL PULP**

VERFAHREN ZUM BLEICHEN VON CHEMISCHEM PAPIERZELLSTOFF

PROCEDE DE BLANCHIMENT DE PULPE CHIMIQUE

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(56) References cited:
EP-A- 0 373 107 **EP-A- 0 383 999**
EP-A- 0 406 617 **WO-A-91/05908**

- **TAPPI JOURNAL**, 11, 1987, pp. 55-61, **L. TENCH et al**, "Oxygen bleaching practices and benefits: an overview"
- **KANTELINEN**, "Entsyymeilako eroon kloorista?" (With enzymes free from chlorine?), **KEmia-Kemi**, vol. 15, pp. 228-231, 1988
- **L. VIIKARI et al**, "Bleaching with enzymes", **Int. Conf. Biotechnolog. Pulp & Paper Ind.**, Stockholm, 1986, pp. 67-69
- **L. VIIKARI et al**, "Application of enzymes in bleaching", **4th Int. Symposium on Wood and Pulping Chemistry**, Paris, 1987, pp. 151-154
- **F. H. DEKKER et al**, **Advances in Carbohydrate Chemistry and Biochemistry**, 1976, vol. 32, p. 278
- **ANDREWS et al**, **Peroxide Bleaching, Kraft Pulp, The Bleaching of Pulp**, Tappi Press, 1963, pp. 237-243
- **C. J. Alfthan et al**, **Svensk. Papperstid.**, vol. 80, no. 15, pp. 480-482, "High temperature peroxide bleaching of sulfate pulp", 1977
- **T. J. McDONOUGH**, **Tappi Journal**, 6, pp. 46-52, "Oxygen bleaching processes", 1986

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Description

The present invention relates to a process for the bleaching of chemical pulp as set forth in the preamble of claim 1.

Especially the chemical pulp obtained by sulfate cooking is brown in color, which is mainly due to lignin remaining in the pulp. Lignin is removed by bleaching, which is usually a multiple-step process in which the pulp is treated alternately with oxidizing chemicals which decompose lignin and with chemicals which dissolve the substances produced as products of the decomposition. The most commonly used oxidizing chemicals have been chlorine-containing substances and oxygen, whereas alkali solutions have been used as chemicals removing the decomposition products.

When reacting, the chlorine-containing bleaching chemicals convert the lignin present in the pulp into organic chlorine compounds, which will pass into the bleaching effluents removed from the pulp. The bleaching effluents constitute an environmental problem owing to the potential toxicity of the organic chlorine compounds passing into the effluents, and also the values of chemical oxygen consumption in the bleaching effluents are detrimentally high.

The bleaching effluents which load the environment the worst are produced in the washing steps following the first chlorination and the first alkali step of the bleaching. Efforts have been made to decrease the load by various methods, for example by replacing the chlorine gas with chlorine dioxide or by using oxygen as the oxidizing chemical in the first step. However, fully satisfactory results have not been achieved by these methods. Efforts to decrease the quantities of chlorophenols and other toxic chlorine compounds in the effluents have indeed been successful, but the values of chemical oxygen consumption of the effluents have not decreased. Therefore, effective biological purification has been needed to back up the said methods.

In recent investigations it has been observed that by using enzymes as an aid in bleaching it is possible to separate lignin and/or hemicellulose from cellulose and to make the pulp in this manner easier to bleach in the subsequent bleaching steps. According to WO-A-89/08738, the residual chlorine content of a pulp bleached by using chlorine chemicals can also be decreased by an enzyme treatment. It is proposed that the enzyme treatment should in this case be carried out either before the oxidation and alkali steps of the bleaching or after them.

The object of the present invention is to provide a new method, based on enzyme treatment of pulp, by which pulp can be bleached in such a manner that the need for bleaching chemicals decreases and at the same time the chemical oxygen consumption and toxicity of the bleaching effluent decrease so that the need for water purification will be smaller. It is characteristic of the invention that the pulp is treated with an enzyme, selected from hemicellulase, cellulase, pectinase and esterase, in two separate enzyme treatment steps of the bleaching process, wherein the pulp subsequent to each enzyme treatment step is treated in an oxidation step.

According to the invention it has thus been observed that the action of enzymes is enhanced when they are used in two different steps. It has been noted that an enzyme treatment carried out at the beginning of the bleaching step enables the amount of chlorine chemicals used to be decreased by approx. 25 %, and thus the repeated enzyme treatments according to the invention will result in considerably higher savings in bleaching chemicals.

In order to minimize the amount of organic chlorine compounds in effluents and in the obtained bleached chemical pulp, it is advantageous to use oxygen and/or hydrogen peroxide and/or chlorine dioxide in the oxidation steps of the process. By this procedure the amount of organic chlorine compounds in the effluents can be decreased by more than 90 % also in the bleaching of softwood pulp, which has not been possible by using the prior-art methods.

According to one preferred embodiment of the invention, at least one enzyme treatment step is followed in the process by a treatment with alkali, in which an oxidizing chemical, such as oxygen or peroxide, is used besides the alkali. It has been observed that such an oxidizing alkali treatment decreases especially effectively the need for chlorine chemicals in bleaching.

In the bleaching process according to the invention, the enzyme treatments break down the hemicellulose and/or lignin present in the pulp and make the pulp more porous, thus increasing the action of the chemicals in subsequent pulp treatment steps. The enzyme treatment may be followed by a washing of the pulp, removing constituents broken down from the pulp; these constituents can be led to a burning so that they will cause no effluent load but the energy contained in them can be exploited in the energy supply of the mill.

With the exception of the enzyme treatment steps, the pulp bleaching according to the invention can be carried out in the conventional manner so that the oxidation and alkali steps alternate. After the various steps the pulp can be washed in order to remove the bleaching chemicals and the broken-down constituents.

According to the invention, the enzyme treatment is preferably carried out within a temperature range of 10-90 °C, preferably within 40-80 °C, and at a pH of 3.3-11.0, preferably 4.0-10.0. The enzyme used may be hemicellulase, cellulase, pectinase, esterase, or a mixture of the same. Hemicellulases are particularly preferred.

It is possible to use one and the same enzyme, such as hemicellulase, in the enzyme treatments belonging to the process according to the invention. It is also possible that the process includes at least two different enzymes.

The invention is described below in greater detail with the help of an embodiment example based on laboratory experiments.

Example

To 300 g of pulp solids obtained from pine sulfate cooking (solids content of pulp 30 %) was added a diluted enzyme mixture Pulpzyme® (Novo, hemicellulase) so as to make the consistency of the pulp 10 % and its xylanase activity 5 U/g of pulp solids. Before this the pH of the pulp had been adjusted by means of acetic acid to a level of 5.5-6.0. The temperature of the enzyme treatment was 55 °C and the treatment time 2 h.

After the enzyme treatment the pulp was washed with water.

Next, the pulp was subjected to an oxidizing bleaching treatment by using a mixture which contained 50 % chlorine dioxide and 50 % chlorine gas. The mixture was proportioned at 2.0 x the kappa number after the pulping. The treatment temperature was 40 °C and the treatment time 45 min and the consistency of the pulp 3.5 %.

Next, the pulp was subjected to an alkali treatment by using a 2-% sodium hydroxide solution the proportion of which was 0.9 x kappa. The consistency of the mixture was 10 %, and the treatment temperature was 60 °C and the treatment time 90 min. After the alkali treatment the pulp was washed with a 20-fold amount of water.

Thereafter the bleaching was continued by repeating the enzyme step by using the same enzyme mixture as in the first step and the oxidation step by using chlorine dioxide and by washing the pulp between the steps as described above. In this case the amount of enzyme in the second enzyme treatment was 2.5 U/g of pulp. The amount of chlorine dioxide in the second oxidizing step was 1.5 % of the amount of the pulp being bleached.

The bleached pulp was analyzed. The results are shown in the following Table 1.

In addition to the experiment (Experiment 2) described above and illustrating the invention, a reference experiment (Experiment 1) was carried but, the results of which are also shown in the following Table 1.

The experiments were carried out as follows:

Experiment 1 (reference experiment): the pulp was not subjected to a second enzyme treatment. In other respects the experiment corresponded to that described above (Experiment 2).

Table 1

	Experiment 1 (reference)	Experiment 2
1st enzyme treatment	1	1
- enzyme proportion (l/t)		
ClO ₂ /Cl ratio	50/50	50/50
Kappa	27.7	27.7
pH		
- enzyme step	5.4	5.6
- oxidation step (ClO ₂ /Cl)	2.1	2.1
- alkali step	11.7	11.6
Consumption of active chlorine (%)	5.54	5.54
Intermediate kappa	5.7	5.7
2nd enzyme treatment (l/t)	-	0.5
pH		
- 2nd enzyme step		5.3
- oxidation step (ClO ₂)	2.1	2.1
- SO ₂ step beginning/end	4.8/3.7	4.8/3.7
Whiteness (ISO)	<u>60.97</u>	<u>67.54</u>

Claims

1. A process for the bleaching of chemical pulp, process which comprises at minimum one oxidation step and at

minimum one alkali treatment step and in which the pulp is treated with an enzyme, **characterized** in that the pulp is treated with at least one enzyme, selected from hemicellulase, cellulase, pectinase and esterase, in two separate enzyme treatment steps of the bleaching process, wherein the pulp subsequent to each enzyme treatment step is treated in an oxidation step.

2. A process according to claim 1, **characterized** in that the oxidizing chemical used in one or several process steps is oxygen.
3. A process according to any of the above claims, **characterized** in that at least one enzyme treatment step is followed in the process by an alkali treatment in which an oxidizing chemical, such as oxygen or peroxide, is used in addition to the alkali.
4. A process according to any of the above claims, **characterized** in that at minimum two different enzymes are used.
5. A process according to any of the above claims, **characterized** in that the process is used for bleaching a pulp obtained from softwood, such as pine sulfate pulp.

Patentansprüche

1. Verfahren zum Bleichen einer chemischen Pulpe, umfassend mindestens einen Oxidationsschritt und mindestens einen Schritt einer alkalischen Behandlung, bei dem die Pulpe mit einem Enzym behandelt wird, dadurch gekennzeichnet, daß die Pulpe in zwei separaten Enzymbehandlungs-Schritten des Bleichverfahrens mit mindestens einem Enzym, ausgewählt aus Hemicellulase, Cellulase, Pectinase und Esterase, behandelt wird, wobei die Pulpe anschließend an jeden der Enzymbehandlungs-Schritt in einem Oxidationsschritt behandelt wird.
2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß es sich bei der in einem oder mehreren Verfahrensschritten verwendeten oxidierenden Chemikalie um Sauerstoff handelt.
3. Verfahren gemäß einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß auf mindestens einen der Enzymbehandlungs-Schritt im Verfahren eine Alkalibehandlung folgt, bei der eine oxidierende Chemikalie, wie Sauerstoff oder Peroxid, zusätzlich zum Alkali verwendet wird.
4. Verfahren gemäß einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß mindestens zwei verschiedene Enzyme verwendet werden.
5. Verfahren gemäß einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Verfahren zum Bleichen einer aus Weichholz erhaltenen Pulpe, wie einer Pinien-Sulfat-Pulpe, verwendet wird.

Revendications

1. Procédé de blanchiment de pâte chimique, qui comprend au minimum une étape d'oxydation et au minimum une étape de traitement alcalin et dans lequel la pâte est traitée de manière enzymatique, caractérisé en ce que la pâte est traitée au moins avec une enzyme, choisie parmi l'hémicellulase, la cellulase, la pectinase et l'estérase, dans deux étapes séparées de traitement enzymatique du procédé de blanchiment, dans lequel la pâte, après chaque étape de traitement enzymatique, est traitée par une étape d'oxydation.
2. Procédé selon la revendication 1, caractérisé en ce que le produit chimique oxydant utilisé dans une ou plusieurs étapes du procédé est l'oxygène.
3. Procédé selon l'une quelconque des revendications ci-dessus, caractérisé en ce que au moins une étape de traitement enzymatique est suivie dans le procédé par un traitement alcalin dans lequel un produit chimique oxydant, comme l'oxygène ou un peroxyde, est utilisé en plus de l'alcalin.
4. Procédé selon l'une quelconque des revendications ci-dessus, caractérisé en ce que au minimum deux enzymes différentes sont utilisées.

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5. Procédé selon l'une quelconque des revendications ci-dessus, caractérisé en ce que le procédé est utilisé pour le blanchiment d'une pâte obtenue à partir de bois tendre, comme la pâte de sapin au sulfate.

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