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(54) PROCESS FOR BLEACHING OF LIGNOCELLULOSE-CONTAINING PULP

VERFAHREN ZUM BLEICHEN VON LIGNOCELLULOSE-ENTHALTENDEM ZELLSTOFF

PROCEDE POUR BLANCHIR LA PATE A PAPIER CONTENANT DE LA LIGNOCELLULOSE

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(56) References cited:
EP-A- 0 402 335
EP-A- 0 415 149
EP-A- 0 535 741
EP-A- 0 578 305
WO-A-92/15752
DE-A- 4 114 135
JP-A- 5 721 591
US-A- 3 867 246
US-A- 4 400 237

- **TAPPI Pulping Conference Proceedings, 1 to 5, November 1992, pp. 1219-1230**
- **The Bleaching of Pulp, TAPPI monograph series n° 27, 1963, pp. 220-223**

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Description

Process for bleaching of lignocellulose-containing pulp

[0001] The present invention relates to a process for bleaching of lignocellulose-containing pulp, in which the pulp is first treated with a complexing agent, then delignified with a peracid or a salt thereof, and subsequently bleached with a peroxide-containing compound. Suitably, delignification is carried out with the strongly oxidising peracetic acid, giving a considerable increase in brightness and a considerable reduction of the kappa number after bleaching with a chlorine-free bleaching agent, such as hydrogen peroxide. The brightness-increasing effect is highly selective, i.e. the viscosity of the pulp is maintained to a comparatively great extent.

Background of the Invention

[0002] Chlorine-free bleaching agents have long been used for bleaching mechanical pulps. In recent years, it has become increasingly common to bleach also chemical pulps with chlorine-free bleaching agents, such as hydrogen peroxide and ozone, even in the first stages. It has been considered necessary to pretreat the pulp immediately after digestion and an optional oxygen-delignifying stage so as to avoid deteriorated pulp properties and an excessive consumption of the bleaching agent. Pretreatment of the pulp primarily involves acid treatment and treatment with a complexing agent or salts of alkaline-earth metals, optionally in combination. Strongly acid pretreatment removes desirable as well as undesirable metal ions from the original positions in the pulp. Treatment with suitable complexing agents primarily removes the undesirable metal ions, while the desirable ones are largely retained. Treatment with salts of alkaline-earth metals maintains or reintroduces the desirable metal ions.

[0003] EP-A-0 415 149 discloses the use of peroxomonosulphuric acid before treatment with oxygen and/or peroxide. The pulp can be pretreated in process stages where heavy metals and organic impurities are removed. In the Examples, the pulp is thus treated in the presence of DTPA at a pH of 2 before treatment with peroxomonosulphuric acid and oxygen. Such an acid wash removes also those metal ions, primarily of alkaline-earth metals, that are necessary for an efficient subsequent bleaching with peroxide-containing compounds or ozone.

[0004] EP-A-0402335 describes a process for improving the effect of an initial alkaline peroxide treatment. The pulp is pretreated with a complexing agent at pH 3.1-9 and a temperature 26°-100°C. The only exemplified peroxide-containing compounds are hydrogen peroxide, and its mixture with oxygen. The purpose of the pretreatment according to EP-A-0402335 is to prepare the pulp for an initial alkaline peroxide treatment.

[0005] WO-A-9215752 describes a process where a pulp is treated with a sequence in two steps. In the first step peroxomonosulphuric acid, i.e. Caro's acid (=an inorganic acid containing sulphur), is added. A complexing agent may be present in the treatment with Caro's acid. In the second step the pulp is bleached with hydrogen peroxide. When a peracid is present along with a complexing agent, i.e. in the same treatment step, the effect of the complexing agent is decreasing dramatically because of the degradation of complexing agents in presence with peracids.

[0006] JP-57-21591 refers to a method of bleaching wood by peracetic acid solution containing hydrogen peroxide, where after the peracetic acid bleaching is finished the remaining hydrogen peroxide is activated by adding alkali.

[0007] DE-A-4114135 discloses a process for bleaching and delignification of pulp comprising treating the pulp with an aqueous solution of an organic peracid and subsequently subjecting the pulp with an alkaline hydrogen peroxide solution activated by cyanamide or cyanamide salt.

[0008] US 3867246 relates to chlorine-free bleaching of cellulose comprising bleaching in a first step with a peroxide under alkaline conditions and then in a second step with a percarboxylic acid under acid conditions and then in a third step again with peroxide under alkaline conditions.

[0009] With increasingly stringent environmental standards, there is a growimg need for completely chlorine-free processes for delignifying and bleaching lignocellulose-containing pulps. To produce fully bleached pulps with unaltered strength properties in a reasonable number of stages and with a reasonable consumption of the bleaching agents, it has become necessary to consider using also powerful, and hence difficultly-controlled, bleaching agents having a high delignifying and/or bleaching capacity.

Description of the Invention

[0010] The invention provides a process in which a lignocellulose-containing pulp is delignified and bleached under the conditions disclosed in the appended claims, whereby a good delignifying and bleaching effect is obtained even before bleaching with a peroxide-containing compound, ozone or sodium dithionite.

[0011] The inventive process comprises bleaching of lignocellulose-containing pulp with a peroxide-containing compound, wherein, before said bleaching, in a sequence is first treated with a complexing agent at a pH in the range of from 3.5 up to about 11 and at a temperature in the range of from 26°C up to about 100°C and then delignified with

an organic peracid or salts thereof at a temperature in the range of from 50°C up to about 140°C, wherein a washing is carried out after the treatment with a complexing agent and before the delignification with an organic peracid or salt thereof at a pH of at least about 4 and that the pulp, before said bleaching, is washed at a pH of at least about 4 whereby the share of peracid added in the delignifying stage to the total amount of peracid and hydrogen peroxide added in the delignifying and bleaching stages, is less than about 60 % on a weight-to-weight basis.

[0012] The inventive process has made it possible to delignify the pulp after treatment with a complexing agent without adversely affecting the conditions, optimised by the treatment with a complexing agent, for the subsequent chlorine-free bleaching, taking into consideration the desirable and undesirable metal ions. Thus, ions of alkaline-earth metals, especially when in their original positions in the pulp, are known to have a favourable effect on the selectivity in bleaching and the consumption of chlorine-free bleaching agents, such as peroxide-containing compounds and ozone.

[0013] In the invention, peracid or salts thereof include organic peracids or salts thereof. As organic peracid, use is made of aliphatic peracids, aromatic peracids or salts thereof. Suitably, peracetic acid or performic acid is used. Sodium is suitably used as cation in the salts, since such salts normally are inexpensive and sodium occurs naturally in the chemical balance in the pulp mill. Peracetic acid or salts thereof are preferred, being advantageous in terms of production and use. In addition, peracetic acid has limited corrosiveness. Any wastewater containing, inter alia, the degradation products of peracetic acid can be easily used for washing or recycled to the chemical recovery system.

[0014] According to the present process, peracetic acid can be produced by reacting acetic acid and hydrogen peroxide, giving what is known as equilibrium peracetic acid, by distilling equilibrium peracetic acid to remove hydrogen peroxide, acetic acid and sulphuric acid, or by reacting acetic acid anhydride and hydrogen peroxide directly in the bleaching stage, giving what is known as in situ peracetic acid. Atypical equilibrium peracetic acid contains about 42% of peracetic acid and about 6% of hydrogen peroxide, i.e. the weight ratio of peracetic acid to hydrogen peroxide is here about 7: 1. When equilibrium peracetic acid is used in the present process, the weight ratio between peracetic acid and hydrogen peroxide can be in the range of from about 10:1 to about 1:60, suitably from 7:1 to 1:15 and preferably from 2.8:1 to 1:2.

[0015] The added amount of peracid or salts thereof, should be in the range of from about 1 kg up to about 100 kg per tonne of dry pulp, calculated as 100% peracid or salt thereof. Suitably, this amount lies in the range of from 2 kg up to 45 kg per tonne of dry pulp, preferably in the range of from 3 kg up to 25 kg per tonne of dry pulp, calculated as 100% peracid or salt thereof.

[0016] Suitably, delignification with peracid or salts thereof is carried out at a pH in the range of from about 2.5 up to about 12. In preferred embodiments where delignification is carried out with peracetic acid, the pH suitably lies in the range of from 3 up to 11, preferably in the range of from 5.5 up to 9. Delignification with the other peracids or salts thereof mentioned above is carried out within the normal pH ranges for the respective bleaching agents, these being well-known to those skilled in the art.

[0017] In the pulp, manganese ions, inter alia, have a particularly adverse effect on the bleaching with chlorine-free bleaching agents, such as alkaline peroxide compounds or ozone. Thus, compounds forming strong complexes with various manganese ions are primarily used as complexing agents. Such suitable complexing agents are nitrogenous organic compounds, primarily nitrogenous polycarboxylic acids, nitrogenous polyphosphonic acids and nitrogenous polyalcohols. Preferred nitrogenous polycarboxylic acids are diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA), DTPA and EDTA being especially preferred. Diethylenetriaminepentaphosphonic acid is the preferred nitrogenous polyphosphonic acid. Also other compounds can be used as complexing agents, such as polycarboxylic acids, suitably oxalic acid, citric acid or tartaric acid, or phosphonic acids. Further, such organic acids as are formed during the pulp treatment with, inter alia, chlorine-free bleaching agents can also be used as complexing agents.

[0018] The pH in the treatment with a complexing agent is of decisive importance in removing the undesirable trace metal ions while at the same time retaining the desirable alkaline-earth metal ions. A suitable pH range depends, inter alia, on the type and the amount of trace metal ions in the incoming pulp. In the inventive process, however, the treatment with a complexing agent should be carried out at a pH in the range of from 3.5 up to about 11, suitably from 3.5 up to 10, and preferably from 4.5 up to 9. A pH within the range of from 5 up to 7 is especially preferred.

[0019] The temperature in the treatment with a complexing agent is of considerable importance for removal of the undesirable trace metal ions. Thus, the content of manganese ions decreases with increasing temperature in the treatment with a complexing agent, which gives an increase in brightness and a reduction of the kappa number. For instance, when the temperature is increased from 20°C to 90°C, the viscosity is also found, surprisingly, to increase noticeably. The treatment with a complexing agent is carried out at a temperature of from 26°C up to about 120°C, suitably from 26°C up to about 100°C, preferably from 40°C up to 95°C, and most preferably from 55°C up to 90°C.

[0020] The added amount of complexing agent depends on the type and amount of trace metal ions of the incoming pulp. Also, this amount depends on the type of agent used as well as the conditions in the treatment with the complexing agent, such as temperature, residence time and pH. However, the added amount of complexing agent should be in

the range of from about 0.1 kg up to about 10 kg per tonne of dry pulp, calculated as 100% complexing agent. Suitably, the amount lies in the range of from 0.3 kg up to 5 kg per tonne of dry pulp, and preferably in the range of from 0.5 up to 1.8 kg per tonne of dry pulp, calculated as 100% complexing agent.

[0021] In preferred embodiments where the delignification with peracid as well as the treatment with a complexing agent are carried out at a close to neutral pH, the need of pH adjustment is minimised. As a result, also the spent liquors from the bleaching and treatment stages can be used internally for washing. This gives a small total volume of wastewater, enabling a considerably more closed system in the pulp mill.

[0022] Bleaching with a peroxide-containing compound, can be carried out in an optional sequence or mixture. The peroxide-containing compound consists of inorganic peroxide compounds, such as hydrogen peroxide or peroxomonosulphuric acid (Caro's acid). Preferably, the peroxide-containing compound is hydrogen peroxide or a mixture of hydrogen peroxide and oxygen.

[0023] When hydrogen peroxide is used as bleaching agent, the pulp can be treated at a pH of from about 7 up to about 13, suitably at a pH of from 8 up to 12, and preferably at a pH of from 9.5 up to 11.5. Bleaching with the other bleaching agents indicated above takes place within the normal pH ranges for the respective agents, these being well-known to those skilled in the art.

[0024] The inventive process may also include a bleaching stage with a peroxide-containing compound before the delignification with peracid or salts thereof.

[0025] The inventive process is carried out with a washing stage before the bleaching with a peroxide-containing compound, such that the washing is carried out at a pH of at least about 4. Washing efficiently removes the complexed trace metal ions that have an adverse effect on the subsequent bleaching with a peroxide-containing compound, primarily manganese ions but also ions of e.g. copper and iron. Because the pH in the washing stage is at least about 4, the alkaline-earth metal ions that have a favourable effect on the subsequent chlorine-free bleaching, primarily magnesium and calcium ions, are retained in the pulp. The pH in the washing stage lies suitably in the range of from 5 up to about 11, preferably in the range of from 6 up to 10.

[0026] Washing before the bleaching with a peroxide-containing compound, is carried out after the treatment with a complexing agent and before the delignification with peracid or salts thereof. In this way, the complexed trace metal ions are efficiently removed, while at the same time the remaining peracid or peroxide-containing compound, if any, can be used in the subsequent bleaching stage. When washing has to be particularly effective, it is possible to have a washing stage after the treatment with a complexing agent as well as after the delignification with peracid or salts thereof.

[0027] The washing liquid may be fresh water, optionally with an addition of a pH-adjusting chemical, or wastewater from one or more bleaching stages or extraction stages, in such a way that a suitable pH in the washing stage is obtained. Furthermore, the washing liquid may consist of other types of optionally purified wastewater, provided it has a low content of undesirable metal ions, such as manganese, iron and copper.

[0028] Washing relates to methods for displacing, more or less completely, the spent liquid in the pulp suspension to reduce its content of, inter alia, dissolved trace metal ions in said suspension. The washing methods may entail an increase of the pulp concentration, e.g. by sucking-off or pressing, but also a reduction of the pulp concentration, e.g. by dilution with washing liquid. Also, washing relates to combinations and sequences in which the pulp concentration is alternately increased and reduced, one or more times. In the present process, a washing method is chosen, which removes not only dissolved organic substance, but also the trace metal ions released in the treatment with a complexing agent, while taking into account what is suitable in terms of process technique and economy.

[0029] Washing efficiency may be given as the amount of liquid phase displaced, as compared with the liquid phase present in the pulp suspension before washing. The total washing efficiency is calculated as the sum of the efficiency in each washing stage. Thus, after a treatment stage, dewatering of the pulp suspension from, say, 10% to 25% pulp concentration gives a washing efficiency of 66.7%. After a subsequent washing stage in which the pulp is first diluted to 3% and then dewatered to 25%, the total washing efficiency is 96.9% with regard to soluble impurities. Washing efficiency should, in the present process, be at least about 75%, suitably in the range of from 90% up to 100%, and preferably in the range of from 92% up to 100%. It is especially preferred that the washing efficiency lies in the range of from 96% up to 100%.

[0030] By using the inventive process the conditions for the chlorine-free bleaching, are optimised such that a high brightness, kappa number reduction and viscosity are achieved with a minimum consumption of the chlorine-free bleaching agent. This is possible without the use of any auxiliary chemicals, such as stabilisers and protective agents, in the chlorine-free bleaching. The remaining bleaching chemicals, such as hydrogen peroxide and alkali, are advantageously used directly in the bleaching stage, in the peracid stage or in some other suitable stage, such that an optimum combination of process technique and production economy is obtained.

[0031] It is also within the scope of the invention, that the delignification with peracid or salts thereof can be reinforced by an addition of such peroxide-containing compounds as have been indicated above. Suitably, such reinforcement is carried out with hydrogen peroxide or a mixture of hydrogen peroxide and oxygen.

[0032] Lignocellulose-containing pulp relates to pulps containing fibres that have been separated by chemical or mechanical treatment, or recycled fibres. The fibres may be of hardwood or softwood. Chemical pulp relates to pulps digested according to the sulphate, sulphite, soda or organosolv process. Mechanical pulp relates to a pulp produced by refining chips in a disc refiner (refiner mechanical pulp) or by grinding logs in a grinder (groundwood pulp). Lignocellulose-containing pulp also relates to pulps produced by modifications or combinations of the above-mentioned methods or processes. Such pulps include thermomechanical, chemimechanical and chemi-themnomechanical pulps. Suitably, the lignocellulose-containing pulp consists of chemically digested pulp, preferably sulphate pulp. It is especially preferred that the lignocellulose-containing pulp consists of sulphate pulp of softwood.

[0033] The inventive process can be applied to pulps with a yield of up to about 90%, suitably in the range of from 30% up to 80%, and preferably in the range of from 45% up to 65%.

[0034] The inventive process can be carried out in an optional position in the bleaching sequence, e.g. immediately after the production of the pulp. When the inventive process is applied to chemically digested pulp, this is preferably delignified in an oxygen stage before the treatment with a complexing agent.

[0035] The inventive process can be applied to chemically digested pulps having an initial kappa number in the range of from about 2 up to about 100, suitably from 5 up to 60, and preferably from 10 up to 40. The kappa number is then measured according to the SCAN-C 1:77 Standard Method.

[0036] In the inventive process, the treatment with a complexing agent should be carried out for a period of time of from about 1 min up to about 960 min, suitably from 15 min up to 240 min, and preferably from 35 min up to 120 min. The pulp concentration in the treatment with a complexing agent may be from about 1% by weight up to about 60% by weight, suitably from 2.5% by weight up to 40% by weight, preferably from 3.5% by weight up to 25% by weight and most preferably from 5.5% by weight up to 25% by weight.

[0037] In the inventive process, delignification with peracid should be carried out at a temperature of from 50°C up to about 140°C, and suitably from 50°C up to about 120°C. Preferably the pulp is delignified at a temperature of from 50°C up to about 100°C and more preferably from 50°C up to 90°C. A temperature in the range of from 50°C up to 80°C is especially preferred. Delignification with peracid should be carried out for a period of time from about 1 min up to about 960 min, suitably from 10 min up to 270 min, and preferably from 30 min up to 150 min. The pulp concentration in the delignification with peracid may be from about 1% by weight up to about 70% by weight, suitably from 3% by weight up to 50% by weight, preferably from 8% by weight up to 35% by weight and most preferably from 10% by weight up to 30% by weight.

[0038] When the bleaching agent used is hydrogen peroxide, the pulp should be treated at a temperature of from about 30°C up to about 140°C, and suitably from about 30°C up to about 120°C. Preferably the pulp is treated at a temperature of from about 30°C up to about 100°C and more preferably from 60°C up to 90°C, and for a period of time of from about 5 min up to about 960 min, suitably from 60 min up to 420 min, and preferably from 190 min up to 360 min. When the bleaching agent used is hydrogen peroxide, the pulp concentration may be from about 1% by weight up to about 70% by weight, suitably from 3% by weight up to 50% by weight, preferably from 8% by weight up to 35% by weight and most preferably from 10% by weight up to 30% by weight. Treatment with the other bleaching agents indicated above takes place within the normal ranges as to temperature, time and pulp concentration for the respective agents, these being well-known to those skilled in the art.

[0039] In preferred embodiments using hydrogen peroxide as bleaching agent, the amount of hydrogen peroxide added in the bleaching stage should be in the range of from about 1 kg up to about 60 kg per tonne of dry pulp, calculated as 100% hydrogen peroxide. The upper limit is not critical, but has been set for reasons of economy. Suitably, the amount of hydrogen peroxide lies in the range of from 6 kg up to 50 kg per tonne of dry pulp, and preferably in the range of from 13 kg up to 40 kg per tonne of dry pulp, calculated as 100% hydrogen peroxide.

[0040] The share of peracid added in the delignifying stage to the total amount of peracid and hydrogen peroxide added in the delignifying and bleaching stages, should be less than about 60% on a weight-to-weight basis. Here, the amount of peracid has been recalculated as 100% hydrogen peroxide. When recalculating peracetic acid as hydrogen peroxide, 1 kg of peracetic acid is equivalent to 0.45 kg of hydrogen peroxide.

[0041] After treatment with a complexing agent, delignification with peracid and subsequent bleaching with a peroxide-containing compound, the pulp can be used for direct production of paper. Alternatively, the pulp may be finally bleached to a desired higher brightness in one or more stages. Suitably, final bleaching is also carried out by means of such chlorine-free bleaching agents as are indicated above, optionally with intermediate extraction stages which can be reinforced by peroxide and/or oxygen. In this way, the formation and discharge of AOX is completely eliminated. It is also possible to use chlorine-containing bleaching agents, such as chlorine dioxide, in the final bleaching and yet obtain a very limited formation and discharge of AOX, since the lignin content of the pulp has been considerably reduced by the present process.

[0042] The invention and its advantages will be illustrated in more detail by the Examples below which however, are only intended to illustrate the invention without limiting the same. The percentages and parts stated in the description, claims and Examples, refer to percent by weight and parts by weight, respectively, unless otherwise stated. Further-

more, the pH values given in the description, claims and Examples refer to the pH at the end of each treatment, unless otherwise stated.

[0043] In the Examples below, the kappa number, viscosity and brightness of the pulp were determined according to the SCAN Standard Methods C 1:77 R, C 15-16:62 and C 11-75:R, respectively. The consumption of hydrogen peroxide and peracetic acid were established by titration with sodium thiosulphate, and potassium permanganate and sodium thiosulphate, respectively.

Example 1

[0044] Oxygen-delignified sulphate pulp of softwood having a kappa number of 16.0, a brightness of 37.1% ISO and a viscosity of 1010 dm^3/kg was treated with EDTA in accordance with the invention, delignified with peracetic acid, and bleached with hydrogen peroxide, in order to illustrate the importance of the pretreatment for the pulp properties after the present process. The pulp was treated with 2 kg EDTA per tonne of dry pulp at a temperature of 90°C, a residence time of 60 min, a pulp concentration of 10% by weight and varying pH. The amount of peracetic acid added was 22.4 kg per tonne of dry pulp, calculated as 100% peracetic acid. In the delignification with peracetic acid, the pH was 5.5-5.9, the temperature 70°C, the treatment time 60 min, and the pulp concentration 10% by weight. Subsequently, the pulp was bleached with hydrogen peroxide at a temperature of 90°C, a residence time of 240 min and a pulp concentration of 10% by weight. The addition of hydrogen peroxide was 25 kg per tonne of dry pulp, calculated as 100% hydrogen peroxide, and the pH was 10.7-11.6. For comparison, the pulp was treated with 2 kg EDTA per tonne of dry pulp at 25°C and for 30 min at a pH of 6 and 2 (tests 5 and 6). For further comparison, the pulp was treated at a pH of about 2 in the absence of a complexing agent (test 7) and without any pretreatment whatsoever (test 8). After each stage, the pulp was washed with deionised water at a pH of 6.0. At this, the pulp was first dewatered to a pulp concentration of 25% and then diluted to a pulp concentration of 3% by weight. After a few minutes, the pulp was dewatered to a pulp concentration of 25% by weight. Consequently, the total washing efficiency was about 97%. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE I

Pulp properties after the H_2O_2 stage				
Test	pH	Kappa number	Viscosity (dm^3/kg)	Brightness (% ISO)
1	1.9	6.1	790	69.1
2	6.4	4.7	890	81.3
3	9.2	5.0	875	77.4
4	12.1	6.5	800	68.3
5	6.0	5.0	850	77.0
6	2.0	6.2	785	68.5
7	2.0	6.4	752	67.5
8	---	6.5	800	65.0

[0045] It is evident from the Table that the treatment of softwood pulp with a complexing agent in a separate stage and at an elevated temperature and at a pH in the range of from 3.5 up to about 11, results in a substantial reduction of the kappa number and a considerable increase in brightness, as well as a high viscosity.

Example 2

[0046] The oxygen-delignified sulphate pulp of softwood used in Example 1 was treated with EDTA, delignified with peracetic acid and bleached with hydrogen peroxide, in order to illustrate the effect of washing between the separate stages in the sequence. The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 5.7 (test 1). The conditions in the delignification with peracetic acid and the bleaching with hydrogen peroxide were as in Example 1 throughout. In test 1, the pulp was washed in accordance with Example 1, both after the treatment with EDTA and after the delignification with peracetic acid. For comparison, the pulp was treated with 2 kg EDTA per tonne of dry pulp at a pH of 7, a temperature of 25°C and a pulp concentration of 8% by weight and for 10 min (test 2). In test 2, the pulp was dewatered after the treatment with a complexing agent to a pulp concentration of 25% by weight. There was no washing or dewatering after the delignification with peracetic acid in test 2. Washing efficiency was about 97% in test 1 and about 74% in test 2. The results after bleaching with hydrogen peroxide (H_2O_2) appear from the Table below.

TABLE II

Test	Pulp properties after the H_2O_2 stage			Remaining
	Kappa number	Viscosity	Brightness	H_2O_2
		(dm^3/kg)	(% ISO)	(kg/tonne)
1	4.7	885	81.3	9.2
2	6.0	760	70.7	0

[0047] It is evident from the Table that the inventive treatment of softwood pulp with a complexing agent at a high temperature followed by washing, gives a much greater reduction of the kappa number and a much higher increase in brightness with a low consumption of hydrogen peroxide and an essentially maintained strength of the pulp, than does treatment at room temperature followed by dewatering.

Example 3

[0048] The oxygen-delignified sulphate pulp of softwood used in Example 1 was treated with EDTA, detignified with peracetic acid and bleached with hydrogen peroxide, in order to illustrate the effect of peracetic acid and separate stages in the sequence according to the invention. The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 5.7. The conditions in the delignification with peracetic acid were as in Example 1, except that 11.2 kg of peracetic acid was added per tonne of dry pulp. The conditions in the bleaching with hydrogen peroxide were as in Example 1. In test 1, the pulp was treated with EDTA, delignified with peracetic acid and bleached with hydrogen peroxide. In test 2, the pulp was delignified with peracetic acid in the presence of EDTA, whereupon the pulp was bleached with hydrogen peroxide. In the delignification in the presence of EDTA in test 2, the pH was 5.1, the temperature 90°C and the treatment time 1 h. In test 3, the pulp was treated with EDTA, whereupon it was delignified and bleached with peracetic acid in the presence of hydrogen peroxide. In the delignification and the bleaching in test 3, the temperature was 70°C for 1 h, whereupon it was raised to 90°C and kept there for 4 h, the pH being 11.1. For comparison, the pulp was treated with EDTA and bleached with hydrogen peroxide (test 4). After each stage, the pulp was washed in accordance with Example 1. The results after the bleaching with hydrogen peroxide (H_2O_2) appear from the Table below.

TABLE III

Test	Pulp properties after the H_2O_2 stage			Remaining
	Kappa number	Viscosity	Brightness	H_2O_2
		(dm^3/kg)	(% ISO)	(kg/tonne)
1	5.0	910	79.7	10.4
2	8.7	800	74.1	0
3	6.1	840	76.2	9.0
4	7.5	890	74.0	6.6

[0049] It is evident from the Table that softwood pulp treated in accordance with the present invention in separate stages will show a substantial reduction of the kappa number and a considerable increase in brightness with a low consumption of hydrogen peroxide and an essentially maintained pulp strength.

Example 4

[0050] The oxygen-delignified sulphate pulp of softwood used in Example 1 was treated with EDTA, delignified with peracetic acid and bleached with hydrogen peroxide, in order to illustrate the effect of pH in washing on the brightness of the pulp after the bleaching stage. The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 5.7. The conditions in the delignification with peracetic acid were as in Example 1, except that the pH was 6.1. The conditions in the bleaching with hydrogen peroxide were as in Example 1. After each stage, the pulp was washed in accordance with Example 1, except that the pH was varied in the washing after the treatment with a complexing agent. The results after the bleaching with hydrogen peroxide (H_2O_2) appear from the Table below.

TABLE IV

Test	pH	Brightness after the H_2O_2 stage (% ISO)
1	2.4	65.9
2	3.5	72.0
3.	4.1	79.0
4	6.6	82.6
5	9.8	81.4
6	10.7	80.9

[0051] It is evident from the Table that softwood pulp treated in accordance with the present invention shows a substantial increase in brightness.

Example 5

[0052] The oxygen-delignified sulphate pulp of softwood used in Example 1 was treated with EDTA, delignified with peracetic acid and bleached with hydrogen peroxide, in order to illustrate the effect of the weight ratio between peracetic acid and hydrogen peroxide in the equilibrium peracetic acid and the washing efficiency between delignification and bleaching. The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 5.7. The conditions in the delignification with peracetic acid were as in Example 1, except that the pH was 5.2 to 6.3. The conditions in the bleaching with hydrogen peroxide were as in Example 1, except that the amount of added hydrogen peroxide was 30 kg per tonne of dry pulp, calculated as 100% hydrogen peroxide. In tests 1 to 4, the pulp was washed as in Example 1, i.e. with a washing efficiency of about 97%. The washing efficiency was about 67% in test 5. There was no washing or dewatering after the delignification with peracetic acid in test 6. The results after the bleaching with hydrogen peroxide (H_2O_2) appear from the Table below.

TABLE V

Test	PAA:H_2O_2	Washing efficiency	Brightness	
		after PAA	after PAA	after H_2O_2
		(%)	(% ISO)	(% ISO)
1	11.5:1	97	54.1	78.0
2	5.0:1	97	57.1	81.2
3	2.1:1	97	60.0	82.7
4	0.6:1	97	63.1	84.0
5	2.1:1	67	60.0	79.5
6	2.1:1	0	60.0	78.0

[0053] It is evident from the Table that treatment of softwood pulp in accordance with the invention, results in a considerable increase in brightness after delignification with peracetic acid as well as after bleaching with hydrogen peroxide.

Example 6

[0054] Oxygen-delignified sulphate pulp of softwood having a kappa number of 16.5, a brightness of 36.0% ISO and a viscosity of 1010 dm^3/kg was treated with EDTA in accordance with the invention, delignified with peracetic acid, and bleached with hydrogen peroxide, in order to illustrate the importance of the pretreatment pH for the pulp properties after the present process. The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 4.0 (test 1). The peracetic acid was an equilibrium peracetic acid, with a weight ratio between peracetic acid and hydrogen peroxide of 4:1. The amount of peracetic acid added was 5 kg per tonne of dry pulp, calculated as 100% peracetic acid. The conditions in the delignification with peracetic acid were as in Example 1, except that the pH was 5.8-6.1. The conditions in the bleaching with hydrogen peroxide were as in Example 1, except that the addition of hydrogen peroxide was 35 kg per tonne of dry pulp, calculated as 100% hydrogen peroxide, and the pH was 11.2-12.0. For comparison, the pulp was treated with 2 kg EDTA per tonne of dry pulp under the conditions stated above, except that the pH was 3.0, i.e. outside the pH range of the present invention (test 2). After each stage, the pulp was washed

in accordance with Example 1. The results after bleach-ing with hydrogen peroxide appear from the Table below.

TABLE VI

Test	pH	Pulp properties after the H_2O_2 stage		
		Kappa number	Viscosity	Brightness
			(dm^3/kg)	(% ISO)
1	4.0	6.2	860	79.1
2	3.0	7.3	850	64.6

[0055] It is evident from the Table that the treatment of softwood pulp with a complexing agent at a pH of at least 3.5, results in a pulp with superior properties compared to treatment with a complexing agent at a pH which is more acidic.

Example 7

[0056] The oxygen-delignified sulphate pulp of softwood used in Example 6 was treated with EDTA, delignified with peracetic acid, and bleached with hydrogen peroxide (tests 1-2), in order to illustrate the effect of residence time and temperature in the delignification step. The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 5.7. The amount of peracetic acid added was 10 kg per tonne of dry pulp, calculated as 100% peracetic acid. In the delignification with peracetic acid, the pH was 6.0-6.5, the temperature 110°C and the pulp concentration 10% by weight, whereas the residence time was varied. The conditions in the bleaching with hydrogen peroxide were as in Example 1, except that the pH was 11.0-11.1. For comparison, the pulp was delignified at 40°C, i.e. outside the temperature range of the present invention (tests 3-4). After each stage, the pulp was washed in accordance with Example 1. The results after delignification with peracetic acid appear from the Table below.

TABLE VII

Test	Temperature	Residence time	Pulp properties after delignification		
			Kappa number	Viscosity	Brightness
	(°C)	(min)		(dm^3/kg)	(% ISO)
1	110	30	13.2	1005	52.0
2	110	75	12.9	1000	52.1
3	40	60	12.5	1005	49.7
4	40	120	12.0	1025	49.6

[0057] It is evident from the Table that the treatment of softwood pulp with peracetic acid at a temperature in the range of from 50°C up to about 140°C, results in a pulp with superior properties compared to treatment at a lower temperature.

Example 8

[0058] Oxygen-delignified sulphate pulp of softwood having a kappa number of 10.3, a brightness of 41.7% ISO and a viscosity of 1000 dm^3/kg was treated with EDTA, delignified with two types of peracetic acid, and bleached with hydrogen peroxide, in order to illustrate the effect of peracetic acid of various compositions. The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 5.5 and the charge of EDTA was 1.5 kg per tonne of dry pulp. The peracetic acids used were one equilibrium peracetic acid with a weight ratio between peracetic acid and hydrogen peroxide of 4:1 (Equil), and one distilled peracetic acid essentially free of hydrogen peroxide and acetic acid (Dist). With both types of peracetic acid, the added amount was 10 kg per tonne of dry pulp, calculated as 100% peracetic acid. The conditions in the delignification with peracetic acid were as in Example 1, except that the pH was 6-7. The conditions in the bleaching with hydrogen peroxide were as in Example 1, except that the addition of hydrogen peroxide was 35 kg per tonne of dry pulp calculated as 100% hydrogen peroxide, the pH was 11.5 and the temperature 110°C in tests 2 and 4. After each stage, the pulp was washed in accordance with Example 1. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE VIII

Test	Perac. acid	Temp.	Pulp prop. after the H_2O_2 stage			Remaining
			Kappa number	Viscosity	Brightness	H_2O_2
		(°C)		(dm^3/kg)	(% ISO)	(kg/tonne)
1	Dist	90	3.2	810	84.4	14.0
2	Dist	110	2.8	760	86.9	8.4
3	Equil	90	3.4	750	84.0	12.1
4	Equil	110	3.0	700	86.5	7.2

[0059] It is evident from the Table that the treatment of softwood pulp according to the invention, results in a pulp with excellent properties after bleaching in combination with a moderate consumption of bleaching agents in the sequence.

Example 9

[0060] The oxygen-delignified sulphate pulp of softwood used in Example 8 was treated with EDTA, delignified with peracetic acid, and bleached with hydrogen peroxide, in order to illustrate the effect of the total amount of bleaching agents and the distribution of the same between the delignifying (Stage 2) and bleaching stages (Stage 3). The conditions in the treatment with a complexing agent were as in Example 1, except that the pH was 5.5 and the charge of EDTA was 1.5 kg per tonne of dry pulp. The peracetic acid used was a distilled peracetic acid essentially free of hydrogen peroxide and acetic acid. The amount of peracetic acid added was varied between 11 and 80 kg per tonne of dry pulp, calculated as 100% peracetic acid. The conditions in the delignification with peracetic acid were as in Example 1, except that the pH was 6-7. The amount of hydrogen peroxide added was varied between 2 and 30 kg per tonne of dry pulp calculated as 100% hydrogen peroxide. The conditions in the bleaching with hydrogen peroxide were as in Example 1, except that the pH was 11.5. The total amounts of hydrogen peroxide and peracetic acid calculated as 100% hydrogen peroxide were 20 kg per tonne of dry pulp in tests 1-4 and 40 kg per tonne of dry pulp in tests 5-8. The share of peracetic acid (calculated as 100% hydrogen peroxide) in stage 2, is also given as a percentage of the total amount. After each stage, the pulp was washed in accordance with Example 1. The results after bleaching with hydrogen peroxide appear from the Table below.

TABLE IX

Test	Hydrogen peroxide			Prop. after H_2O_2 stage		Remaining
	Stage 2	Stage 3	Stage 2	Viscosity	Brightness	H_2O_2
	(kg/tonne)		(%)	(dm^3/kg)	(% ISO)	(kg/tonne)
1	5	15	25	930	79.9	7.1
2	10	10	50	940	79.5	5.0
3	15	5	75	935	77.2	3.3
4	18	2	90	950	73.0	1.5
5	10	30	25	870	85.3	12.1
6	20	20	50	880	84.9	9.3
7	30	10	75	890	82.5	5.8
8	36	4	90	895	78.0	3.0

[0061] It is evident from the Table that excellent pulp properties are obtainable after delignification and bleaching according to the present invention.

Claims

1. A process for bleaching of lignocellulose-containing pulp with hydrogen peroxide, where the pulp before said bleaching is first treated with a complexing agent at a pH in the range of from 3.5 up to about 11 and at a temperature in the range of from 26°C up to about 100°C, **characterised in that** a washing is carried out after the treatment

with a complexing agent and before the delignification with an organic peracid or salts thereof at a pH of at least about 4, and that the pulp after the treatment is delignified with an organic peracid or salts thereof at a temperature in the range of from 50°C up to about 140°C, and that the pulp after the delignification with the organic peracid or salts thereof and before said bleaching is washed at a pH of at least about 4, whereby the share of peracid added in the delignifying stage to the total amount of peracid and hydrogen peroxide added in the delignifying and bleaching stages, is less than about 60% on a weight-to-weight basis.

2. A process according to claim 1, **characterised in that** the lignocellulose-containing pulp is a chemically digested pulp.

3. A process according to any of the preceding claims, **characterised in that** the peracid is peracetic acid.

4. A process according to any of the preceding claims, **characterised in that** the hydrogen peroxide bleaching is carried out in the presence of oxygen.

5. A process according to any of the preceding claims, **characterised in that** the complexing agent is a nitrogenous organic compound.

6. A process according to any of the preceding claims, **characterised in that** the pulp is delignified at a temperature in the range of from 50°C up to about 120°C, preferably from 50°C up to 80°C.

7. A process according to any of the preceding claims, **characterised in that** the amount of complexing agent added is up to 1.8 kg per tonne of dry pulp, calculated as 100% complexing agent.

8. A process according to any of the preceding claims, **characterised in that** the treatment with a complexing agent is preceded by an oxygen stage.

9. A process according to any of the preceding claims, **characterised in that** the delignification with peracid is carried out at a pH in the range from 5.5 up to 9.

Patentansprüche

1. Verfahren zum Bleichen von lignocellulosehaltigem Zellstoff mit Wasserstoffperoxid, wobei der Zellstoff vor dem Bleichen zuerst bei einem pH-Wert im Bereich von 3,5 bis etwa 11 und bei einer Temperatur im Bereich von 26°C bis etwa 100°C mit einem Komplexierungsmittel behandelt wird, **dadurch gekennzeichnet, daß** das Waschen nach der Behandlung mit dem Komplexierungsmittel und vor der Entholzung mit einer organischen Persäure oder Salzen davon bei einem pH-Wert von mindestens etwa 4 durchgeführt wird, und dass der Zellstoff nach der Behandlung bei einer Temperatur im Bereich von 50°C bis etwa 140°C mit einer organischen Persäure oder Salzen davon entholzt wird, und **dass** der Zellstoff nach dem Entholzen mit der organischen Persäure oder Salzen davon und vor dem Bleichen bei einem pH-Wert von mindestens etwa 4 gewaschen wird, wobei der Anteil der im Entholzungsvorgang zugegebenen Persäure an der Gesamtmenge der Persäure und des Wasserstoffperoxids, die im Entholzungsvorgang zugegeben werden, kleiner als etwa 60 % ist, bezogen auf das Gewicht.

2. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** der lignocellulosehaltige Zellstoff ein chemisch aufgeschlossener Zellstoff ist.

3. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** die Persäure Peressigsäure ist.

4. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** das Bleichen mit Wasserstoffperoxid in Gegenwart von Sauerstoff durchgeführt wird.

5. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** das Komplexierungsmittel eine organische Stickstoffverbindung ist.

6. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der Zellstoff bei einer Temperatur im Bereich von 50°C bis etwa 120°C, vorzugsweise von 50°C bis 80°C, entholzt wird.

7. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** die Menge des zugegebenen Komplexierungsmittels bis 1.8 kg pro Tonne des trockenen Zellstoffs beträgt, berechnet als 100 % Komplexierungsmittel.

8. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** der Behandlung mit einem Komplexierungsmittel ein Sauerstoffschritt vorausgeht.

9. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** das Entholzen mit Persäure bei einem pH-Wert im Bereich von 5,5 bis 9 durchgeführt wird.

Revendications

1. Procédé de blanchiment de pâte à papier contenant de la lignocellulose à l'aide de peroxyde d'hydrogène, dans lequel, avant ce blanchiment, on traite d'abord la pâte avec un agent complexant, à un pH situé dans l'intervalle allant de 3,5 à environ 11 et à une température située dans l'intervalle allant de 26°C à environ 100°C, procédé **caractérisé en ce que** l'on effectue un lavage, après le traitement par un agent complexant et avant la délignification effectuée à l'aide d'un peracide organique ou d'un sel d'un tel composé, à un pH valant au moins environ 4, et après ce traitement, on délignifie la pâte à l'aide d'un peracide organique ou d'un sel d'un tel composé, à une température située dans l'intervalle allant de 50°C à environ 140°C, et **en ce que**, après la délignification effectuée à l'aide d'un peracide organique ou d'un sel d'un tel composé et avant ledit blanchiment, on lave la pâte à un pH valant au moins environ 4, le rapport de la quantité de peracide ajoutée lors de l'étape de délignification à la somme des quantités de peracide et de peroxyde d'hydrogène ajoutées lors des étapes de blanchiment et de délignification valant moins de 60 % environ, en poids/poids.

2. Procédé conforme à la revendication 1, **caractérisé en ce que** la pâte contenant de la lignocellulose est une pâte obtenue par digestion chimique.

3. Procédé conforme à l'une des revendications précédentes, **caractérisé en ce que** le peracide est de l'acide peracétique.

4. Procédé conforme à l'une des revendications précédentes, **caractérisé en ce que** le blanchiment au peroxyde d'hydrogène est effectué en présence d'oxygène.

5. Procédé conforme à l'une des revendications précédentes, **caractérisé en ce que** l'agent complexant est un composé organique azoté.

6. Procédé conforme à l'une des revendications précédentes, **caractérisé en ce qu'**on délignifie la pâte à une température située dans l'intervalle allant de 50°C à environ 120°C, et de préférence de 50°C à 80°C.

7. Procédé conforme à l'une des revendications précédentes, **caractérisé en ce que** la quantité d'agent complexant ajoutée, calculée en agent complexant à 100 %, peut valoir jusqu'à 1,8 kg par tonne de pâte sèche.

8. Procédé conforme à l'une des revendications précédentes, **caractérisé en ce que** le traitement par un agent complexant est précédé d'un traitement à l'oxygène.

9. Procédé conforme à l'une des revendications précédentes, **caractérisé en ce que** la délignification réalisée à l'aide d'un peracide est effectuée à un pH situé dans l'intervalle allant de 5,5 à 9.