EUROPEAN PATENT APPLICATION

(51) Int Cl.: D21C 3/06, D21C 9/10

Bleached, strong sulfite chemical pulp, a process for the production thereof and products derived therefrom

The present invention relates to a process for preparing a bleached sulfite chemical pulp comprising:

- delignification of chips of a lignocellulosic material in a sulfite pulping process beyond the defibration point of said material until kappa values of below 50 are reached, and
- bleaching of the fibrous material thus obtained by means of a chlorine-free bleaching sequence which comprises at least one first bleaching step with a chlorine-free oxidant in the presence of a base.

The chemical pulp prepared according to this process and paper or nonwoven made from such are characterized by a high degree of brightness (at least 83%, in particular more than 86%) and high strength.
Description

[0001] The present invention relates to a completely bleached and strong sulfite chemical pulp, a process for the production thereof and products made of this pulp (nonwovens or paper, especially tissue paper).

Background Art

[0002] In the production of paper, we differentiate between chemical pulp and mechanical pulp.

[0003] According to DIN 6730, chemical pulp is a fibrous material obtained from plant raw materials from which most non-cellulose components have been removed by chemical pulping without substantial mechanical post-treatment. In case of chemical pulping processes such as the sulfite or sulfate (Kraft) process, primarily the lignin components and the hemi-cellulose components are dissolved from the wood to varying degrees depending on the field of application of the chemical pulp. The result is a fibrous material consisting primarily of cellulose.

[0004] Mechanical pulp is the general term for fibrous materials made of wood entirely or almost entirely by mechanical means, optionally at increased temperatures. Mechanical pulp is subdivided into the purely mechanical pulps (groundwood pulp and refiner mechanical pulp) as well as mechanical pulps subjected to chemical pretreatment: chemo-mechanical pulp (CMP), such as chemo-thermomechanical pulp (CTMP).

[0005] Chemical and mechanical pulp are also known by the general designation pulp.

[0006] The strength of papers made from chemical pulps (hereinafter abbreviated as "strength of the chemical pulp") is substantially determined by the pulping degree of the wood used as starting material. The binding ability of the fibers first increases as more and more lignin is removed and reaches a maximum at a lignin content of about 10%. At this residual lignin content, the fibrous material has good stiffness and resistance to tearing along with a high binding ability. As delignification proceeds, the overall strength of the chemical pulp decreases due to the strong attack of most of the pulping chemicals on the carbohydrate portion (cellulose and hemicellulose) of the wood.

[0007] However, such extensive delignification is accompanied by losses in yield so that, for many years, there have been efforts to develop pulps having higher contents of residual lignin:

- high-yield chemical pulps, according to DIN 6730 a chemical pulp primarily pulped chemically, but subsequently subjected to mechanical defibration;
- semi-chemical pulp, a pulp according to DIN 6730 obtained from plant raw materials by mechanical pulping from which only part of the non-fibrous components have been removed and which is subjected to mechanical post treatment; and
- chemi-mechanical pulps (CMP, CTMP, as defined above).

[0008] In the meantime, the recovery of primary fibers has focused, on the one hand, on the production of mechanical pulps in very high yields by addition of 1% to 5% maximum of sodium sulfite such that hydrophilizing occurs by introducing sulfonic acid groups in conjunction with a low dissolving rate of the wood components, and on the other hand, on the production of full chemical pulps according to the sulfate process.

[0009] If chemical pulp recovered by the sulfate process (called "Kraft pulp" or "sulfate chemical pulp") is to be used for producing products with a high degree of brightness, the lignin must be removed completely, since even small amounts of residual lignin are discolored due to chemical changes in the lignin structure (primary condensation). This is largely carried out in a pulping process. Any residual lignin still present is then removed in several bleaching steps.

[0010] The native lignin is less discolored by the acidic sulfite process. For this reason, it was possible to use high-yield chemical pulps made by acidic or semi-acidic sulfite processes in unbleached form for special applications. If a higher degree of brightness was required, such chemical pulps were also bleached in a delignifying manner with chlorine and bleaching agents containing chlorine. However, these products were unable to satisfy the ever-increasing optical demands. In addition, environmental concerns about bleaching agents containing chlorine and chemical pulps containing chlorine led to a situation where industrial-level production of high-yield chemical pulps was not pursued. Furthermore, less expensive recycling paper has increasingly been used in paper production.

[0011] However, delignifying bleaching of chemical pulps often has the disadvantage that chemicals used for bleaching also attack cellulose fibers to a considerable extent, thus reducing the strength of chemical pulps. Therefore up until now, it has been thought that pulps of sufficient strength and of a high degree of brightness could only be obtained by pulping to low kappa values followed by bleaching. This also applies to the sulfate pulping process.

[0012] A summary of the development of acidic sulfite pulping processes for preparing semi-chemical pulps is found in R. Runkel and K.F. Patt, "Halbzellstoffe" (Semichemical Pulps), Günther-Stalb Verlag, Biberach 1958, pages 35 to 37 and pages 95 to 96. The production of high-yield chemical pulps, semichemical pulps and chemi-mechanical pulps...
according to the sulfite process is also described in "S.A. Rydholm, Pulping Processes, Interscience Publishers, New York, London, Sydney, 1965, pages 418 to 420".

[0013] In addition, G. Jayme, L. Broschinsky, W. Matzke (in Das Papier 18, 1964, pages 308 through 314) present a general survey of high-yield chemical pulps and give a detailed description of rapid pulping in the vapor phase with magnesium bisulfite at a maximum temperature of 180°C over a period of 8 to 20 minutes.

[0014] DE-A-1-517 219 relates to the preparation of a (high-yield) sulfite chemical pulp. Wood raw material is pulped with an aqueous solution containing sulfite and/or bisulfite ions as well as sodium, potassium, magnesium, or ammonium ions. The pH of the solutions at onset of pulping is 3.0 to 7.0, preferably 3.7 to 5.0. The maximum pulping temperature is 140°C to 190°C, preferably 150°C to 170°C. The entire pulping process takes more than 400 minutes. The residence time at the maximum temperature is 30 to 200 minutes. Pulping is carried out at a chlorine number of the finished chemical pulp in the range of 15 to 32, the pulped material then being subjected to controlled defibration and/or defibration/refinement. After that, fines are removed in an amount of 0.2 to 7% of the amount of the chemical pulp.

[0015] In unbeaten form (freeness value \( \text{SR} = 14.5 \) to 15) the material thus obtained has a breaking length of 6.3 km. The chemical pulp is not bleached.

[0016] US 4,634,499 and US 4,734,162 each relate to processes for preparing a chemical pulp from hardwood which is especially suitable for the preparation of tissue papers. Pulping is carried out with ammonium sulfite, first at less than 110°C, then at a maximum temperature of 140°C to 155°C at a pH of about 2 to 3. The chemical pulp is not subjected to an additional bleaching step.

[0017] EP 0 287 960 A relates to a process for preparing a hemicellulose hydrolysate and a special chemical pulp by a two-step process, wherein

- a first step comprises pre-hydrolysis of the ligno-cellulosic materials, for example, with water, a mineral acid, sulfur dioxide, sulfite pulping liquor, and sulfite waste liquor, at a temperature of 100°C to 180°C and over a hydrolysis period of 10 to 200 minutes, and
- a second step in which the lignin contained in the pre-hydrolysed material is dissolved occurs by means of neutral sulfite pulping with addition of anthaquinone as the catalyst, the initial pH being at least 10. The temperature is preferably 160°C to 180°C and the treatment time 100 to 200 minutes.

[0018] Following the second step, the resulting ligno-cellulosic material is mechanically defibrated and optionally bleached.

[0019] Yields obtained in this manner range from 37.0% to 45.7% based on the wood used, the kappa number after cooling ranges from 17.2 to 48.1, and the degree of brightness (ISO value) after bleaching with chlorinated agents at 48.2 to 87.1.

[0020] GB-1,546,877 B relates to a CTMP (chemo-thermomechanical pulp) which is suitable for absorbant products such as tissue paper, and, additionally, has a light color. Yields at 85% to 95% are well above the common values for high yield pulps. The production process comprises the following steps:

- washing of a ligno-cellulosic material with water
- impregnation and pulping with a liquid containing sulfur dioxide at a temperature of 100°C to 170°C, preferably at a pH of 5 to 11.
- partial defibration of the resulting material by mechanical means with simultaneous bleaching.

[0021] Suitable bleaching chemicals are alkali metal peroxides such as sodium peroxide or hydrogen peroxide, or reducing bleaching agents such as dithionite, hydroxyl amine, thiourea, or thioglycolic acid.

[0022] An essential feature of the resulting chemical pulp is a content of at least 10% by weight of sulfonated fiber bundles, each consisting of two to four individual fibers.

[0023] This British patent does not address the strength properties of the chemical pulp obtained. The description of the patent further points to non-satisfactory degrees of brightness of the resulting chemical pulp.

[0024] EP 0 446 110 A describes a process for bleaching chemical pulps (yield ranges approx. 85 to 90%), which are obtained mechanically (chemical pulp), optionally combined with chemical methods (chemomechanical pulp) and/or thermal methods. This bleaching process comprises the following steps:

- pretreatment of (mechanical or chemomechanical) pulp with a complexing agent for metal ions followed by a washing step
• treatment with sulfite and a more electronegative reducing agent at a pH between 7 and 12.5 followed by a washing step

• bleaching treatment with hydrogen peroxide in an alkaline environment.

[0025] According to example 1, this process produces degrees of brightness of 83.9% ISO.

[0026] However, all processes known from the prior art for preparing pulps having a high degree of brightness have disadvantages. In particular, insufficient resistance against fiber collapse and poor strength of individual fibers is observed in the pulp obtained. At low degrees of beating, known pulps often have strength values insufficient for preparation of tissue products.

[0027] Bleached mechanical pulps and bleached chemomechanical pulps have the further disadvantage of an unstable degree of brightness. This is due to the fact that the bleaching chemicals convert chromophoric groups of the lignin into non-chromophoric groups, which however are unstable. This type of reduction in the degree of brightness (discoloration) may be induced either by light or heat.

[0028] A disadvantage of known chemical pulps is their chlorine content and/or formation within the bleach of soluble reaction products containing chlorine, which is environmentally undesirable.

[0029] P. Lengyel and S. Morvay, "Chemie und Technologie der Zellstoffherstellung, Güntter-Staib Verlag Biberach/Riss 1973, pages 370 to 379" teach in the context of bisulfite pulping that the advantageous development of the strength properties of the bisulfite pulp is mainly remarkable at higher yields -approximately 60% - which typically correspond to kappa numbers in the order of 55 to 65. The authors further state that the lignin content of these pulps is too high as to produce a bleached pulp economically. The background for this statement is that bleaching of pulps with high residual lignin content, in particular TCF (total chlorine free) bleaching often requires multi-stage sequences which are costly and complicated and result in a fairly high water consumption. In addition, it is mentioned in this publication that even the subsequent use of peroxides and other bleaching agents does not result in color stability of the bleached pulp.

[0030] Therefore, it is the object of the present invention to make available a pulp that has good strength properties in addition to a high and durable optical quality, making it particularly suitable for the production of nonwovens and paper (products), in particular tissue products.

[0031] A further aspect of the invention is to make available an economic process for producing such pulp.

[0032] A further object of the present invention involves providing a process leading to a suitable balance between bleachability and the properties (of the bleached pulps), such as strength, optical quality and yield obtained.

[0033] Finally, a further object of the present invention is to make available pulp-based paper or nonwovens and/or the corresponding products which are characterized by both resistance to mechanical stress and high quality of appearance.

[0034] It is a further object of the invention to make available an environmentally compatible process for producing environmentally compatible pulp and derivative paper and/or nonwoven products.

SUMMARY OF THE INVENTION

[0035] These objects are achieved by:

• a process for producing a chlorine-free bleached sulfite chemical pulp comprising the following steps:
  delignification of chips (commonly woodchips) from lignocellulosic material by a sulfite pulping process, in particular, in the presence of magnesium until the kappa number of the delignified material has reached a value below 50, and
  bleaching of the resulting fibrous material in a chlorine-free bleaching sequence comprising at least one bleaching step using an oxidizing agent in the presence of a base;

• chlorine-free bleached chemical pulp obtainable by a sulfite pulping process followed by chlorine-free bleaching, characterized in that it has an ISO degree of brightness of at least 83 %, in particular more than 86 % and a strength, expressed as breaking length, of at least 4 km (measured according to Zellcheming V/12/57), determined with a test sheet (ISO 5269-2, August 1998) produced from the pulp after beating the same to a degree of freeness of 25°SR, and

• paper and nonwovens obtainable from this pulp.
DETAILED DESCRIPTION OF THE INVENTION

Process

[0036] In the first step of the process according to the invention, chips (commonly woodchips) from ligno-cellulosic material are partially delignified in a sulfite pulping process, in particular in the presence of magnesium, until kappa values of below 50 (according to DIN 54357, August 1978) are reached. Preferably, the partially delignified fibrous material obtained from the first step has a kappa value of maximally 49, maximally 48, maximally 47, or maximally 46 with increasing preference. Kappa ranges of 30 to 45, in particular 33 to 42 are even more preferred.

[0037] These kappa values are preferably achieved by conducting the delignification beyond the point of defibration of the material. The point of defibration is the point in time during the pulping at which the fibers subjected to chemical delignification may readily be separated into individual fibers without mechanical defibration.

[0038] Once the Kappa values strived for have been reached, the individual fibers are collected generally by pumping off the pulped lignocellulosic material out of the digester.

[0039] As to the typical differences between sulfite and sulfate pulping processes the following can be noted. During the initial pulping phase, sulfite solutions prefer to dissolve lignin in the middle lamella of the wood cells, and thereby the bonding between the wood cells is lost. This results in a fiber surface of relatively low residual lignin content. The largest part of the yet remaining lignin is located in the central layer of the cell wall (S2) (on the structure of a wood cell, see e.g. Figure 20.2, page 509 in T.P. Nevell and S. Haig Zeronian, Cellulose Chemistry and Its Applications, John Wiley & Sons). In contrast to the residual lignin content of sulfate pulp, the residual lignin content of the pulp resulting from the sulfite process, in particular the acidic sulfite process has not only relatively few chromophoric groups, but it is also less condensed and therefore more reactive.

[0040] The term "ligno-cellulosic" material includes all materials containing cellulose and lignin as main components, typically wood. In (dry) wood, the lignin content is generally at least 20 wt.-% (hardwood about 22 wt.%, conifers 27 to 33 wt.-%).

[0041] Usually, the cellulose content of wood is at least 40 wt.-%, generally 40 to 50 wt.-%. Both softwood from conifers and hardwood from deciduous trees may be used in the process of the invention. Examples for suitable kinds of wood comprise softwoods such as spruce or pine, and hardwoods such as aspen, beech, birch, maple, poplar and oak. In addition, eucalyptus is especially suitable as a hardwood source of fibers for soft tissue papers. The use of spruce and beech is especially preferred.

[0042] Prior to pulping, the ligno-cellulosic material used is roughly chopped into chips. The size of the chips may vary and ranges for example from 1 to 5 cm in breadth and length, with a thickness of up to 1.5 cm.

[0043] Pulping (first step) is carried out with an acidic sulfite solution in a known manner, e.g. with an aqueous solution containing sulfite and/or bisulfite ions as well as sodium, potassium, magnesium, or ammonium ions. Suitable methods are described in depth in G. A. Smook, M. J. Kocurek, Handbook for Pulp and Paper Technologists, Tappi, Atlanta, 1982, pages 58 through 65. Preferably, the chemical pulping occurs in a single step, i.e. without sudden (as contrast to gradual) changes in conditions of the process such as pH. The entire pulping process does not require any additional mechanical means, even though this is not excluded by the invention.

[0044] Chips of lignocellulosic material may be pulped in alkaline, neutral, or acidic conditions, however, preferably in an acidic environment with sulfite. Pulping at a pH of 1 to 5, especially 1.2 to 4.0 is particularly preferred.

[0045] In a particularly preferred embodiment, pulping is performed with an aqueous solution containing sulfite and/or bisulfite ions as well as magnesium ions. One advantage of this variant is the possibility of recovering MgO and SO₂ from the pulping waste liquors by thermal decomposition and recycling them to the pulping process. The pulping temperature preferably ranges from 130°C to 165°C, in particular 135°C to 150°C. Until a maximum temperature of 130°C to 150°C is attained, heating should preferably be carried out over a period of 30 to 180 minutes, in particular 70 to 140 min, e.g. 90 to 120 min.

[0046] Then, the temperature is maintained at the maximum temperature preferably for a time period of 160 min to 15 hours (900 min), in particular 3 hours to 12 hours (e.g. 4, 6, 8 or 10 hours). Depending on the type of wood to be delignified, shorter times (e.g. 160 min to 300 min) may suffice. This is for instance the case for hardwood chips such as beech chips, whereas softwood chips as obtained from spruce may require longer times, preferably in the order of from 480 to 720 min. A time period of 30 to 60 minutes is preferred for cooling from the maximum temperature (T_max) to room temperature.

[0047] Total pulping time (heating + pulping at T_max + cooling) ranges preferably from 220 to 1140 minutes.

[0048] The SO₂ content of the pulping solution relative to the dry weight (see Examples for its determination) of the lignocellulosic material used preferably equals 5 to 30 % by weight, in particular 15 to 24 % by weight. The proportion of magnesium if present, relative to the dry weight of the lignocellulosic material, expressed as "active MgO", preferably equals 4 to 10 % by weight, in particular 5 to 8.5 % by weight (e.g. 6.5%). The "active MgO" content can be measured by chloramine titration.
According to the invention, addition of further pulping chemicals such as, for example, anthraquinone is not required.

The lignocellulosic material-to-liquor ratio preferably ranges from 1:1.5 to 1:5, relative to the dry weight of the lignocellulosic material. For some types of softwoods, such as spruce, lower ratios in the order of 1:1.5 to 1:3 may be most suitable, whereas particularly good results for hardwood such as beech were obtained with a ratio of from 1:3.5 to 1:4.5.

The first step of the pulping process according to the invention results in an unbleached chemical pulp (hereinafter also referred to as "fibrous material"), which is then transferred to the bleaching sequence.

The yield of unbleached chemical pulp relative to the dry weight of the ligno-cellulosic material used is often less than 55 % by weight, can be (depending on the type of wood) less than 50 weight %, but preferably amounts to at least 40 % by weight, in particular at least 45 % by weight.

The degree of brightness of the material thus obtained is preferably more than 45% ISO, more preferably 50 to 75% ISO, even more preferably at least 55 to 70% ISO, in particular more than 60% ISO (e.g. more than 65% ISO).

Preferably, the unbleached chemical pulp has the following strength parameters, each measured according to ISO 5269-2; August 1998, on test sheets having a basis weight of about 75 g/m² using a standard climate according to DIN EN 20187 (see description in the Examples). All of the following values are based on beaten chemical pulp which corresponds to a freeness value (°SR, measured according to DIN-ISO 5267/1; March 1999) of approx. 25:

- a breaking length (dry, measured according to Zellcheming V/12/57) of at least 6 km, more preferably at least 7 km, e.g. 10 km, and
- a tear strength (dry, see Examples, measured according to Elmendorff; DIN 53128) relative to 100 g/m², of at least 50 cN, in particular at least 65 cN, e.g. 75 cN.

According to preferred embodiments, the above dry breaking length values are at least 9 km, more preferably at least 9.5 km, e.g. 10.5 km for softwood pulps such as spruce pulp; and at least 6 km, more preferably at least 7 km, e.g. 7.5 km for hardwood pulps, such as beech pulp.

Preferred tear strength (dry) values for softwoods such as spruce are at least 65 cN, more preferably at least 70 cN, e.g. 75 cN; preferred values for hardwood such as beech are at least 50 cN, more preferably at least 53 cN, e.g. 57 cN.

The sulfite pulping process used as the first step of the process of the invention has the advantage over the sulfate process of producing a pulp having a relatively light color even at higher residual lignin contents.

Prior to bleaching, the chemical pulp resulting from the first stage (delignification) is separated from the cooking liquor in a known manner, e.g. it may be filtered and preferably washed (usually with water).

The common feature of each bleaching sequence used according to the invention is bleaching with a chlorine-free oxidant, in the presence of a base in a so-called "first bleaching step". The entire bleaching sequence is carried out with chlorine-free agents. The terms "chlorine-free bleaching sequence" and "chlorine-free bleaching chemicals" mean that the bleaching chemicals contain no chlorine, neither elemental chlorine, nor chlorine-containing compounds such as, e.g. in chlorine dioxide.

The entire bleaching sequence is preferably carried out without additional mechanical pulping means, i.e. defibration means.

The entire bleaching sequence may comprise one, two, three or more bleaching steps.

However, according to the invention it is preferred to reduce the number of bleaching steps as far as possible. It is thus preferred that the entire bleaching sequence does not contain more than three bleaching steps, more preferably not more than two bleaching steps. If three or two bleaching steps are to be carried out, each step includes preferably only oxidative bleaching agents (rather than reducing conditions as obtained with formamidinosulfonic acid or dithionite).

The base used in the first bleaching step is preferably the same base that is used in pulping. This makes it easier to close water cycles, since the filtrate from the washer after the first bleaching step may be used for washing in the washer after the pulping step. Furthermore, by using the same base, preferably one containing magnesium, the resulting bleach waste liquors may be disposed together with the cooking waste liquors or at least partially recycled. Further economic advantage could be taken from recycling the filtrates in the bleaching stage itself, therefore utilising the residual peroxide in the bleaching stage.

Sodium hydroxide, magnesium oxide (MgO), and/or magnesium hydroxide (Mg(OH)₂) are preferred bases. (Herein the term "Magnesium oxide (MgO)" also includes the use of magnesium hydroxide (Mg(OH)₂)). Hydrogen peroxide (H₂O₂) is a preferred oxidant. The amount of oxidant is preferably 30 to 60 kg/t, in particular 35 to 55 kg/t, relative to the fibrous material used. (If not stated otherwise, kg/t always refers to the dry weight of the fibrous material treated). The amount of base used preferably ranges from 10 to 50, in particular 15 to 25 kg/t relative to the fibrous
In an additional embodiment (referred to as an acidic wash or "A Q"), one sets the pH of the pulp suspension at a value of 3 or less, e.g. by addition of H₂SO₄. In this manner, one may dissolve MgO that has precipitated onto the pulp or into the suspension. After setting the pH value, one adds the complexing agent to the suspension.

Preferably, the amounts of stabilizing silicate range from 0.5 to 10 kg/t relative to the fibrous material used. Preferably, the complexing treatment is performed at higher temperature, preferably at 50 to 70°C. Its duration depends on the temperature used. Most suitably it ranges from 10 min to 60 min.

- In one embodiment, the complexing treatment is carried out in a weakly acidic environment, e.g. at pH values from 4 to 6 (hereinafter referred to as "Q").
- In order to activate the residual lignin content of the fibrous material, one may also use an oxidant in an acidic environment along with the complexing agent. For this purpose, peracetic acid (hereinafter referred to as "Q/PAA") and ozone are particularly suited.
- In an additional embodiment (referred to as an acidic wash or "A Q"), one sets the pH of the pulp suspension at a value of 3 or less, e.g. by addition of H₂SO₄. In this manner, one may dissolve MgO that has precipitated onto the pulp or into the suspension. After setting the pH value, one adds the complexing agent to the suspension.

Among these embodiments, the "Q" type complexing technique is most preferred.

An alternative technique of stabilizing bleaching oxidants, in particular hydrogen peroxide in the presence of a base, such as NaOH or in particular MgO involves the use of water-soluble silicates during the bleaching step. It is preferred to use water-soluble sodium and potassium silicate solutions which are known as "water-glass". Preferably the water-glass has a molar ratio of 2 to 4 mol SiO₂ per mol alkali oxide. It is further possible and preferred to combine the two stabilizing techniques explained, i.e. to conduct a bleaching treatment followed by an oxidative bleaching step in the presence of water-soluble silicates (this applies in particular to the use of hydrogen peroxide as oxidant). Preferably, the amounts of stabilizing silicate range from 0.5 to 10 kg/t fibrous material, in particular from 1 to 7 kg/t. Of course, lower amounts of oxidants (e.g. lower amounts of hydrogen peroxide) in a second oxidative bleaching step also require lower amounts of stabilizing silicate.

Further, it is preferred to conduct an acid treatment ("A") prior to an oxidative bleaching step, in particular between two oxidative bleaching steps. Without being bound to theory, it is believed that this acid treatment contributes
to a lower profile of transition metal traces in the pulp and therefore increases the efficiency of subsequent oxidative steps, in particular if these are performed with hydrogen peroxide.

[0077] For the acid treatment, a non-oxidizing, chlorine-free acid, such as sulphuric acid is taken. It is preferred to add from 10 to 50 kg/t, in particular from 20 to 40 kg/t acid to the fibrous material. It has proven beneficial to conduct the acid treatment above room temperature (20°C), preferably at temperatures ranging from 30 to 80°C, in particular 40 to 70°C. The duration of this acid treatment is typically from 30 minutes to 180 minutes, preferably from 30 to 90 minutes. The acid treatment is preferably conducted at pH values ranging from 2.5 to 3.5.

[0078] The second (optional) bleaching step may be followed by additional oxidizing bleaching steps with chlorine-free oxidants in the presence of base. This third oxidizing bleaching can be performed under the same conditions as those described in the second bleaching step, but preferably with even lower amounts of oxidant and shorter durations.

[0079] The above oxidizing bleaching steps can be combined with a so-called "reducing bleaching step" using a reducing bleaching agent, even though this is not preferred. Bleaching agents that are suitable for the reducing bleaching step include water-soluble dithionite salts, hydroxylamine, thiourea, thioglycolic acid, borohydride (e.g. sodium borohydride), or formamidin sulfonic acid. Especially preferred is the use of formamidin sulfonic acid or dithionite, particularly sodium dithionite. The amount of reducing agent used in the reducing bleaching step may range from 5 to 15 % by weight relative to the amount of fibrous material used. This reaction can be performed at a pH ranging from 9 to 11. Sodium hydroxide or magnesium oxide can be used to set the pH. Magnesium oxide has the advantage that the spent filtrate of this step may be utilized together with pulping spent liquor. Usable temperatures for the reaction are in the range of 80° to 95° C. The reaction preferably takes from 60 to 90 minutes.

[0080] The total residence time of the pulp in all bleaching steps (including acid or complexing treatments) ranges preferably from 200 to less than 700 minutes, e.g. maximally 650 min, more preferably from 250 to 600 minutes, in particular from 300 to 500 minutes.

[0081] All steps of the bleaching sequence are preferably carried out in an aqueous slurry at fibre consistencies of from 1 to 15 weight%, based on the dry weight of the fibres. Consistencies of from 1 to 5 weight % are preferred for the complexing treatment. The other treatments are more preferably carried out at consistencies ranging from 5 to 15 weight%.

[0082] Following each individual step of the bleaching sequence (including acid or complexing treatments), the fibrous material is preferably separated from the bleaching solution, e.g. by filtration, and washed. In this manner, the consumption of chemicals in bleaching may often be reduced. By washing upon completion of the bleaching sequence, the purity of the pulp according to the invention may be increased. Furthermore, it is preferred to work countercurrent, i.e. to wash the completely bleached fibrous material with clean water and to use the resulting wash water for pulp of the previous bleaching step or steps. Finally, the wash water from the washing following the first bleaching step is preferably used for washing the pulp following the pulping process. It is possible in the cases described above to use fresh water in addition to the wash water that is led in countercurrent.

[0083] Selection and sequence of the bleaching steps may be varied, where with multi-step bleaching sequences it is preferred to begin the bleaching sequence with an oxidative bleaching of the type PMgO (bleaching step with hydrogen peroxide in the presence of MgO as base).

[0084] If softwood, such as spruce is to be bleached, it is preferred to use not more than two oxidative bleaching steps. Accordingly, the bleaching may also be conducted in one oxidative bleaching step, preferably hydrogen-peroxide-based bleaching step. The available results indicate further, that it may be of advantage to combine two oxidative bleaching steps as described above, in particular hydrogen peroxide-based bleaching steps.

[0085] The most preferred bleaching sequences for softwoods, such as spruce involve:

1) PMgO/S
2) Q - PMgO, or
3) PMgO/S - A - PNaOH/S' 

[0086] The present inventors have further found out that one oxidative bleaching step is sufficient to efficiently bleach hardwoods, such as beech, if this bleaching steps follows the delignification procedure explained above. As regards the bleaching of hardwoods, it is particularly preferred to employ bleaching sequences as follows:

4) PMgO/S
5) Q - PMgO, or
6) PNaOH/S, or
7) Q - PNaOH' 

wherein the symbols mean the following:
As seen from the above bleaching sequences, it is generally preferred to stabilize peroxide-based bleaching steps by using a preceding complexing treatment (Q) and/or adding silicate (S) to the hydrogen peroxide.

Based on the most recent knowledge, bleaching sequences 3, 4 and 6 represent the best mode for practicing the invention.

In the manner described above, one may obtain bleached chemical pulp having the properties of a chemical pulp that is obtained by a sulfite pulping process, in particular a magnesium (bi)sulfite process, and that is then bleached without the use of chlorine or chlorine-containing chemicals. The pulp according to the invention has a brightness of at least 83% ISO. Moreover, the invention preferably pertains to pulp having a degree of brightness of more than 86% ISO, for instance at least 86.2% ISO, more preferably at least 86.5% ISO, in particular at least 86.8% ISO, e.g. 88%, 89% or 90% ISO.

The pulp according to the invention is further characterized by a breaking length (dry) of at least 4 km, and with increasing preference at least 5 km, at least 6 km, at least 7 km, at least 8 km, and at least 9.5 km, e.g. 10 km measured according to Zellcheming V/12/57 on a test sheet made from beaten pulp (freeness of 25° SR measured according to DIN-ISO 5267/1; March 1999) basis weight of approx. 75 g/m², produced according to ISO 5269-2; August 1998, in a standard climate according to DIN EN 20187; November 1993). For pulps derived from softwood, such as spruce, preferred breaking length (dry) values are at least 7 km, preferably at least 8 km, more preferred at least 9 km, in particular at least 10 km, e.g. 10.5 km. According to preferred embodiments for pulps derived from hardwood, such as beech, the breaking length (dry) is at least 4 km, preferably at least 5 km, even more preferred at least 5.5 km, even more preferred at least 6 km, e.g. 6.5 km.

One advantage of the pulp according to the invention is that in contrast to mechanical pulp or chemomechanical pulp, its degree of brightness does not significantly decline during further processing and usage.

The pulp according to the invention is substantially free of chlorine and/or chloride. Preferably, the pulp has an OX content of less than 30 mg/kg, or in particular, is free of OX. The OX content relates to the residual halogen organic compounds in the pulp, which may essentially be formed during bleaching and are measured in accordance with DIN 38414/18 and PTS-RH012/90.

Pulp that is low in OX or is OX-free, and/or products derived from such pulp are more environmentally compatible than pulp and pulp-derived products containing OX. This also applies to the production process. In order to close water cycles as much as possible, it is likewise preferred that only chlorine-free chemicals be used in pulp production, because that way a build-up of chlorine, chloride, and/or chlorine-containing substances may be avoided.

These properties of the pulp make it especially suitable for the production of tissue paper.

Preferably, the bleached, unbeaten pulps according to the invention have:

- a tear strength (dry, measured according to Elmendorff (DIN 53128)) relative to 100 g/m² of at least 40 cN, e.g. 130 cN.
- tear index (dry, measured according to DIN 53128) of at least 3.5 mNm²/g, e.g. 13 mNm²/g.
- a tensile index (dry, measured according to Zellcheming V/12/1957) of at least 40 Nm/g, e.g. 65 Nm/g.

These values refer to test sheets which were produced as described above under breaking length, except for using unbeaten bleached pulp having a degree of freeness of about 12 to 14°SR.

For bleached, unbeaten softwood pulp, such as spruce pulp the following preferred values can be given:

- a tear strength relative to 100 g/m² of at least 100 cN, more preferably of from 110 to 130 cN;
- tear index of at least 10 mNm²/g, more preferably from 10 to 13 mNm²/g;
- a tensile index of at least 55 Nm/g, more preferably from 55 to 65 Nm/g;

and bleached unbeaten hardwood pulp, such as beech pulp preferably has the following strength parameter:
• a tear strength relative to 100 g/m² of at least 40 cN, more preferably 50 to 55 cN;
• tear index of at least 3.5 mNm²/g, more preferably 3.5 to 4.2 mNm²/g;
• a tensile index of at least 40 Nm/g, more preferably 40 to 50 Nm/g;

whereby these values are measured as indicated above and in the experimental section.

[0098] The (bleached) pulp according to the invention preferably has a very low fiber bundle content of bundles having at least two fibers, i.e. preferably less than 1 % by weight relative to the dry weight. It is more preferred for it to be free of such bundles.

[0099] The residual lignin content of the bleached pulp according to the invention (measured according to DIN 54357, August 1978) ranges preferably from 10 to 29, more preferably from 12 to 25, in particular from 12 to 20. For softwood, such as spruce preferred kappa values range from 12 to 25, in particular from 15 to 20. Preferred values for hardwood, such as beech are from 10 to 20, more preferably from 12 to 18, in particular from 13 to 17.

[0100] One may estimate the residual lignin content by multiplying the kappa numbers by 0.15. A kappa number of 20, which lies within the inventive range, thus corresponds to a residual lignin content of approx. 3 % by weight.

[0101] The process according to the invention thus makes it possible to a large extent to delignify lignocellulosic material in very short bleaching sequences. This is possible without the aid of mechanical pulping means.

[0102] The average fiber length of the inventive bleached pulp ranges preferably from 1.8 to 2.2 mm (measured according to Kajaani using a Kajaani machine FS-200).

[0103] The water retention capacity of the pulp according to the invention ranges preferably from 130 to 150 %, in particular from 140 to 145 % (measured according to Zellcheming IV/33/57, as described in the Examples).

Paper or Nonwoven (Product)

[0104] The present invention also relates to paper or nonwoven comprising the bleached pulp according to the invention, preferably in the amount of at least 50 % by weight, in particular at least 80 % by weight, relative to the dry weight of the finished product.

[0105] The paper can be a packaging paper, a graphic paper or tissue paper. Preferably, the paper is a tissue paper.

[0106] The tissue paper or nonwoven may be one-ply or multiple-ply.

[0107] The German terms "Vlies" and "Vliesstoffe" are applied to a wide range of products which in terms of their properties are located between the groups, paper, paperboard, and cardboard on the one hand and the textile products on the other, and are currently summarized under the term "nonwovens" (see ISO 9092 - EN 29092). The invention allows the application of known processes for producing nonwovens, such as what are called air-laid and spun-laid techniques, as well as wet-laid techniques.

[0108] Nonwovens may also be called textile-like composite materials, which represent flexible porous fabrics that are not produced by the classic methods of weaving warp and weft or by looping, but by intertwining and/or by cohesive and/or adhesive bonding of fibers which may for example be present in the form of endless fibers or prefabricated fibers of a finite length, as synthetic fibers produced in situ or in the form of staple fibers. The nonwovens according to the invention may thus consist of mixtures of synthetic fibers in the form of staple fibers and the pulp according to the invention.

[0109] "Papers" are also planar materials, albeit essentially composed of fibers of a plant origin and formed by drainage of a fibrous-material suspension on a wire or between two continuously revolving wires and by subsequent compression and drainage or drying of the thus produced fibrous mat (cf. DIN 6730, May 1996). The standard restricts the range of mass per unit area (basis weight) for paper to a maximum of 225 g/m².

[0110] Depending on the type of paper, the production process comprise also a sizing and/or smoothing step, along with the typical process steps of sheet formation, pressing, and drying described above.

[0111] Based on the underlying compatibility of the production processes (wet laying), "tissue" production is counted among the paper making techniques. The production of tissue is distinguished from paper production by its extremely low basis weight of normally less than 50 g/m² and its much higher tensile energy absorption index. (In processing inventive pulp to tissue paper, one generally selects a basis weight of 8 to 30 g/m², especially 10 to 25 g/m² per ply. The total basis weight of multiple-ply tissue products is preferably equal to a maximum of 65 g/m², more preferably to a maximum of 50 g/m².) The tensile energy absorption index is arrived at from the tensile energy absorption index in which the tensile energy absorption is related to the test sample volume before inspection (length, width, thickness of sample between the clamps before tensile load). Paper and tissue paper also differ in general with regard to the modulus of elasticity that characterizes the stress-strain properties of these planar products as a material parameter.

[0112] A tissue's high tensile energy absorption index results from the outer or inner creping. The former is produced by compression of the paper web adhering to a dry cylinder as a result of the action of a crepe doctor or in the latter instance as a result of a difference in speed between two wires ("fabrics"). This causes the still moist, plastically deformable paper web to be internally broken up by compression and shearing, thereby rendering it more stretchable.
under load than an uncreped paper. Most of the functional properties typical of tissue and tissue products result from the high tensile energy absorption index (see DIN EN 12625-4 and DIN EN 12625-5).

One example of papers and paper products is represented by hygiene papers, particularly tissue papers and hygiene products (tissue products) made therefrom and which are e.g. used in personal grooming and hygiene, the household sector, industry, the institutional field in a wide variety of cleaning processes. They are used to absorb fluids, for decorative purposes, for packaging or even as supporting material, as is common for example in medical practices or in hospitals.

In a preferred embodiment, the pulp is refined prior to formation. Preferably, the resulting pulp has a freeness value of more than 15, in particular more than 16 and simultaneously not more than 26 °SR. With an increased freeness value there is an increase in breaking length. It is further preferred to refine only long fibres as occurring in softwood. According to a further preferred embodiment, a mixture of unrefined hardwood short fibres and refined softwood long fibres is used to prepare the aqueous slurry which is then supplied to the formation part of the paper machine.

This additional surface treatment (beating), which has a favorable effect on the strength properties of the resulting paper/tissue paper, may preferably be brought about within the pulp refinement system of a paper/tissue paper machine. In another preferred embodiment, such surface treatment (beating) occurs as part of pulp production, i.e. while it is still at the pulp plant. A refiner is particularly suitable for this purpose. Fibrillation of the surface occurs during mechanical treatment of the pulp/water suspension. This treatment influences the static and dynamic strength properties.

Depending on the refiner’s operating mode, the fibers are shortened (cut) or are fibrillated, which includes the separation of the outer layers of the fiber wall, this latter process substantially increasing the surface and bonding capacity of the fibers. The refiner operating mode associated with fibrillation is therefore preferred.

Paper can be formed by placing the fibers, in an oriented or random manner, on one or between two continuously revolving wires of a paper making machine while simultaneously removing the main quantity of water of dilution until dry-solids contents of usually between 12 and 35 % are obtained.

Drying the formed primary fibrous web occurs in one or more steps by mechanical and thermal means until a final dry-solids content of usually about 93 to 97 %. In the case of tissue making, this stage is followed by the crepe process which crucially influences the properties of the finished tissue product in conventional processes. The conventional dry crepe process involves creping on a usually 4.5 to 6 m diameter drying cylinder, the so-called yankee cylinder, by means of a crepe doctor with the aforementioned final dry-solids content of the raw tissue paper (wet creping can be used if lower demands are made of the tissue quality). The creped, finally dry raw tissue paper (raw tissue) is then available for further processing into the paper product or tissue paper product according to the invention.

Instead of the conventional tissue making process described above, the invention gives preference to the use of a modified technique in which an improvement in specific volume is achieved by a special kind of drying within process section b and in this way an improvement in the bulk softness of the thus made tissue paper is achieved. This process, which exists in a variety of subtypes, is termed the TAD (through air drying) technique. It is characterized by
the fact that the "primary" fibrous web (like a nonwoven) that leaves the sheet making stage is pre-dried to a dry-solids content of about 80% before final contact drying on the yankee cylinder by blowing hot air through the fibrous web. The fibrous web is supported by an air-permeable wire or belt and during its transport is guided over the surface of an air-permeable rotating cylinder drum. Structuring the supporting wire or belt makes it possible to produce any pattern of compressed zones broken up by deformation in the moist state, resulting in increased mean specific volumes and consequently leading to an increase in bulk softness without decisively decreasing the strength of the fibrous web.

[0125] Another possible influence on the softness and strength of the raw tissue lies in the production of a layering in which the primary fibrous web to be formed is built up by a specially constructed headbox in the form of physically different layers of fibrous material, these layers being jointly supplied as a pulp strand to the sheet making stage.

[0126] When processing the raw fibrous web or raw tissue paper into the final product (third process section), the following procedural steps are normally used individually or in combination: cutting to size (longitudinally and/or cross cutting), producing a plurality of plies, producing mechanical ply adhesion, volumetric and structural embossing, ply adhesion, folding, imprinting, perforating, application of lotions, smoothing, stacking, rolling up.

[0127] To produce multi-ply tissue paper products, such as handkerchiefs, toilet paper, towels or kitchen towels, an intermediate step preferably occurs with so-called doubling in which the raw tissue in the finished product's desired number of plies is usually gathered on a common multiply master roll.

[0128] The processing step from the raw tissue that has already been optionally wound up in several plies to the finished tissue product occurs in processing machines which include operations such as repeated smoothing of the tissue, edge embossing, to an extent combined with full area and/or local application of adhesive to produce ply adhesion of the individual plies (raw tissue) to be combined together, as well as longitudinal cut, folding, cross cut, placement and bringing together a plurality of individual tissues and their packaging as well as bringing them together to form larger surrounding packaging or bundles. The individual paper ply webs can also be pre-embossed and then combined in a roll gap according to the foot-to-foot or nested methods.

EXAMPLES

[0129] In the description of the invention and in the following examples the following test methods were used to evaluate the chemical pulps according to the invention.

1) Producing the test sheets
   From the pulps to be measured test sheets (having a basis weight of approx. 75 g/m²) were made in accordance with ISO 5269-2: August 1998). Before being tested in terms of physical properties e.g. by means of the tensile test, the thus obtained test sheets were always conditioned for a duration of at least 12 hours in a standard climate at a temperature of (23±1)° C and a relative humidity of (50±2)% in accordance with DIN EN 20187; November 1993, paper, cardboard and pulp, a standard climate for pretreatment and testing and a method of monitoring the climate and pretreatment of samples, November 1993 (see ISO 187 : 1990).

2) Breaking length (Dry)
   The breaking length was determined using a dry test sheet produced according to 1) following a process described in Zellcheming V/12/1957.

3) Tear Strength (Dry) according to Elmendorff
   Tear strength was determined according to Elmendorff using a test sheet produced according to 1) following a process described in DIN 53128.

4) Tensile index (dry)
   Tensile index was determined using a test sheet produced according to 1) following a process described in Zellcheming V/12/1957.

5) Tear index (dry)
   Tear index was determined using a test sheet produced according to 1) following a process described in DIN 53128.

6) Kappa number
   The kappa number is determined according to DIN 54357 (August 1978)

7) WRV (water retention value)
   The WRV is determined in the following way.
The principle of determining the WRV is based on centrifuging swollen pulp samples at room temperature in a special-purpose centrifuge beaker with 3000-fold gravitational acceleration. The WRV in percent (mass portions in percent) indicates the portion of water in the sample that cannot be centrifuged. The implementation followed the German Zellcheming Code of Practice IV/33/57 (issued on January 1, 1957).

- A fibrous material treated with excess water as a swelling agent is taken.
- The tubes for the centrifuge inserts are filled to about 2/3 of the volume with the moist pulp sample without pressing firmly.
- A triple determination is to be performed each time.
- The tubes are inserted into the centrifuge beaker.
- Centrifuging conditions: 15 min at 4800 rpm
- After the centrifuge comes to a standstill, the tubes are taken out and the centrifuged substance immediately transferred with the aid of pincers as completely as possible into the weighing bottles previously dried at 103 °C and tared at room temperature where they are weighed (remove glass spheres beforehand)
- The samples are now dried for at least 6 hours in the circulating-air drying cabinet, immediately seal when taking them out and allow them to cool in the desiccator. Now reweigh.

The calculation is made on the basis of the following equation:

\[
WRV = \left( \frac{W-D}{D} \right) \times 100
\]

where \( W \) = the weight of the moist substance, \( D \) represents the dry weight of the substance; and \( W \) minus \( D \) = the weight of the absorbed water.

8) Dry Weight (oven-dried)

The weight values that are given as "dry weight" or "oven-dried" relate to dried material, lignocellulosic material, pulp, paper, or nonwoven (product) that was dried at 105 °C until constant weight was achieved.

9) Freeness value
The freeness value (in °SR) was measured according to DIN-ISO 5267/1; March 1999.

10) Degree of Brightness
The degree of brightness (in %) was determined according to ISO following SCAN C11:1975.

Example 1

[0130] Unless otherwise stated, the amounts given in kg/t and the consistency values (in %) in the following Examples consistently refer to the dry weight of the pulp treated.

[0131] Spruce chips of a length of 13 to 35 mm and with a thickness of 1 to 10 mm were pulped in a magnesium bisulfite solution (SO₂ as hydrogen sulfite or sulfite-bound SO₂) having a total SO₂ content of 16% by weight/wood (dry weight) and a magnesium content (measured as active MgO) of 5,0 % by weight/wood (dry weight) at an initial pH of 4,0 and temperature of 146 °C. The wood-to-liquor ratio was 1:2. Heating to the maximum temperature of 146 °C took 120 minutes. The temperature was maintained at the maximum level for a total of 10 hours (600 minutes). The resulting pulp was separated from spent liquor, washed with water, and dried, yielding approximately 54 % (dry weight) relative to the wood used, at a kappa number of 37,0 and a degree of brightness of 67,5 % ISO. The breaking length of the unbeaten (= freeness value of 14° SR), unbleached pulp was 8,2 km.

[0132] The washed pulp was not subjected to a complexing treatment. Instead the pulp was immediately bleached in aqueous solution containing 50 kg of hydrogen peroxide and 18 kg MgO/oven-dried pulp (at a consistency of 11 %) for a reaction time of 210 minutes and at a reaction temperature of 80° C. Additionally 3 kg/t of sodium silicate/oven-dried pulp was added to stabilise the hydrogen peroxide against degradation. The brightness after the first bleaching stage (PMgO) was approximately 83 % ISO.
The washed pulp was subsequently subjected to an acidic treatment, being conducted at a temperature of 50°C for a period of 60 minutes with 30 kg/t of sulfuric acid at a consistency of 9%. The pulp was then bleached in aqueous solution containing 30 kg/t of hydrogen peroxide and 15 kg/t NaOH (at a consistency of 13%) for a reaction time of 120 minutes and at a reaction temperature of 78°C. The aqueous solution contained 1.5 kg sodium silicate/oven-dried pulp, added to stabilise the peroxide against degradation.

Example 2

Beech chips of a length of 15 to 30 mm and with a thickness of 3 to 8 mm were pulped in a magnesium bisulfite solution (free SO2 as hydrogen sulfite or sulfite-bound SO2) having a total SO2 content of 18% by weight/wood (dry weight) and a magnesium content (measured as active MgO) of 5.7% by weight/wood (dry weight) at an initial pH of 4.2 and temperature of 150°C. The wood-to-liquor ratio was 1:4. Heating to the maximum temperature of 150°C took 90 minutes. This temperature was maintained at the maximum level for a total of 3.35 hours (210 minutes). The resulting pulp was separated from spent liquor, washed with water, and dried, yielding 48.8% (dry weight) relative to the wood used, at a kappa number of 39.6 and a degree of brightness of 59.6% ISO. The tensile index of the beaten (= freeness value of 25°SR), unbleached pulp was 76.2 Nm/g at a tear index of 5.9 mNm²/g.

Example 3

Beech chips of a length of 15 to 30 mm and with a thickness of 3 to 8 mm were pulped in a magnesium bisulfite solution (free SO2 as hydrogen sulfite or sulfite-bound SO2) having a total SO2 content of 18% by weight/wood (dry weight) and a magnesium content measured as active MgO of 5.7% by weight/wood (dry weight) at an initial pH of 4.2 and temperature of 150°C. The wood-to-liquor ratio was 1:4. Heating to the maximum temperature of 150°C took 90 minutes. This temperature was maintained at the maximum level for a total of 3.35 hours (210 minutes). The resulting pulp was separated from spent liquor, washed with water, and dried, yielding 49.1% (dry weight) relative to the wood used, at a kappa number of 39.6 and a degree of brightness of 59.6% ISO. The tensile index of the beaten (= freeness value of 25°SR), unbleached pulp was 76.2 Nm/g at a tear index of 5.9 mNm²/g.

Example 4

Beech chips of a length of 15 to 30 mm and with a thickness of 3 to 8 mm were pulped in an acid magnesium sulfite solution (free SO2 as hydrogen sulfite or sulfite-bound SO2) having a total SO2 content of 20% by weight/wood (dry weight) and a magnesium content measured as active MgO of 4.4% by weight/wood (dry weight) at an initial pH of 1.7 and temperature of 138°C. The wood-to-liquor ratio was 1:4. Heating to the maximum temperature of 138°C took 90 minutes. This temperature was maintained at the maximum level for a total of 3.0 hours (180 minutes). The degree of brightness of the resulting pulp was determined to be 87.0% ISO. The fully bleached pulp had a breaking length of 6 km in an unbeaten state (freeness value = 14°SR).
resulting pulp was separated from spent liquor, washed with water, and dried, yielding 49.9 % (dry weight) relative to the wood used, at a kappa number of 39.0 and a degree of brightness of 46.8 % ISO. The tensile index of the beaten (= freeness value of 25° SR), unbleached pulp was 71.5 Nm/g at a tear index of 4.9 mNm²/g.

The washed pulp subsequently was subjected to complexing treatment by bringing the same into contact with 2 kg/t of complexing agent DTPA at a consistency of 3 % at a temperature of 60° C for a period of 30 minutes. The pH value was set at 5.2 for the complexing treatment with H₂SO₄. Then the pulp was washed and bleached in aqueous solution containing 40 kg/t of hydrogen peroxide and 40 kg/t NaOH (at a consistency of 10 %) for a reaction time of 360 minutes and at a reaction temperature of 70° C. This aqueous solution contained 5 kg/t of sodium silicate to stabilise the hydrogen peroxide against degradation. The peroxide consumption was 69.8 % of charge.

The degree of brightness of the resulting pulp was determined to be 86.0 % ISO. The yield (dry weight) of the pulp obtained after the bleaching sequence was 92.2 % by weight relative to the dry weight of the pulp subjected to the bleaching sequence. The bleached pulp had a tensile index of 57.7 Nm/g and a tear index of 6.1 mNm²/g in a beaten state (freeness value = 25°SR).

The pulp, which is pulped and bleached according to the invention, and/or any paper produced from such are characterized by an excellent combination of degree of brightness and strength properties. In contrast to other pulp having similar residual lignin contents, the pulp according to the invention has a high stability in degree of brightness.

In accordance with the invention, this advantageous combination of properties can be reached in very short bleaching sequences.

**Claims**

1. A process for preparing bleached sulfite chemical pulp, comprising the following steps:

   delignification of chips of a lignocellulosic material in a sulfite pulping process until the kappa number (residual lignin content) of said material has reached values below 50, and

   bleaching of the fibrous material thus obtained by means of a bleaching sequence which is performed exclusively with chlorine-free reagents and comprises at least a first bleaching step with a chlorine-free oxidant in the presence of a base.

2. A process according to claim 1 wherein the residual lignin content following the step of delignification and prior to bleaching in terms of the kappa number is between 30 and 45.

3. A process according to claim 1 or 2, wherein sulfite pulping is conducted under acidic conditions.

4. A process according to any one of the claims 1 through 3 wherein sulfite pulping is conducted in the presence of magnesium in an acidic environment.

5. A process according to one of the previous claims 1 through 4 wherein sulfite pulping is conducted with an aqueous solution containing magnesium bisulfite, optionally an excess of SO₂, at a temperature of 130° to 165° C and at a pH of 1 to 5.

6. A process according to claim 1 wherein the reaction sequence for chlorine-free bleaching of pulp comprises at least one additional bleaching step with a chlorine-free oxidant in the presence of a base.

7. A process according to claim 1 or 6, wherein the oxidant used in the bleaching step(s) is hydrogen peroxide.

8. A process according to claim 1 or 6, wherein the base used in the bleaching step(s) is sodium hydroxide or magnesium hydroxide or oxide.

9. A process according to one of claims 1 or 6 through 8, wherein prior to treatment with an oxidant, treatment with a metal ion complexing agent is conducted.

10. A process according to one of claims 1 or 6 through 8, wherein the oxidative bleaching step(s) is (are) preceded by an acid treatment at elevated temperature.

11. A process according to one of claims 1 or 6 through 10, wherein the oxidative bleaching step(s) are carried out in the presence of a water-soluble silicate.
12. A process according to one of claims 1 or 6 through 11, wherein the reaction sequence for chlorine-free bleaching of pulp does not comprise more than two bleaching steps, said steps using oxidants for bleaching.

13. A process according to one of claims 1 or 6 through 12, wherein the entire residence time for the bleaching sequence (including optional complexing or acid treatments) is from 200 to 650 min.

14. A process according to one of claims 1 or 6 through 13, wherein the chips of lignocellulosic material are softwood chips, in particular spruce chips and the bleaching sequence comprises one or two bleaching steps in total, said bleaching steps using hydrogen peroxide for bleaching.

15. A process according to claim 14, wherein the bleaching sequence comprises one bleaching step in total, said bleaching step using magnesium oxide or hydroxide as base and being preceded by a complexing treatment.

16. A process according to claim 14 or 15, wherein during bleaching with hydrogen peroxide a water-soluble silicate is used as stabilizer.

17. A process according to claim 14, wherein the bleaching sequence comprises two bleaching steps in total, said bleaching steps being separated by an acid treatment at elevated temperature.

18. A process according to one of claims 1 or 6 through 13, wherein the chips of lignocellulosic material are hardwood chips, in particular beech chips and the bleaching sequence comprises only one bleaching step in total, said bleaching step using hydrogen peroxide for bleaching.

19. A process according to claim 18, wherein said bleaching step is preceded by a complexing treatment.

20. A chemical pulp, obtainable by a sulfite pulping process and subsequent chlorine-free bleaching, characterized in that it has a degree of brightness of at least 83% ISO and a test sheet produced after beating the pulp (freeness of 25°SR according to DIN-ISO 5267/1) has a strength, expressed as breaking length (measured according to Zellcheming V/12/57), of at least 4 km.

21. A chemical pulp according to claim 20, wherein the pulp has a degree of brightness of more than 86% ISO.

22. A chemical pulp according to claim 20 or 21, wherein the pulp is a softwood pulp, in particular spruce pulp and has a breaking length of at least 5.5 km.

23. A chemical pulp according to claim 20 or 21, wherein the pulp is a hardwood pulp, in particular beech pulp and has a breaking length of at least 4 km.

24. A chemical pulp according to claim 20 or 21, wherein the pulp has a kappa number of between 10 and 29.

25. A chemical pulp according to claim 20, 21 or 22, wherein the pulp is a softwood pulp, in particular spruce pulp and has a kappa number of between 15 and 20.

26. A chemical pulp according to claim 20, 21 or 23, wherein the pulp is a hardwood pulp, in particular beech pulp and has a kappa number of between 12 and 18.

27. A chemical pulp according to any of the claims 20 through 26, wherein it is subjected to a beating step following bleaching.

28. A paper or nonwoven prepared from a chemical pulp according to any of the claims 20 through 27.

29. A paper according to claim 28 which is tissue paper.
## DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int.Cl.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>EP 0 402 335 A (EKA NOBEL AB) 12 December 1990 (1990-12-12) * example 8 *</td>
<td>1,7-10, 12,15, 20,21,28</td>
<td>D21C3/06, D21C9/10</td>
</tr>
<tr>
<td>X</td>
<td>EP 0 512 590 A (EKA NOBEL AB) 11 November 1992 (1992-11-11) * the whole document *</td>
<td>1,2, 6-14, 18-21,28</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>US 5 916 415 A (MILLER WILLIAM J) 29 June 1999 (1999-06-29) * the whole document *</td>
<td>1,6-8, 12,20,21</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>US 4 450 044 A (FRITZVOLD BJORN H ET AL) 22 May 1984 (1984-05-22) * claims 1,2,5-10; example 3 *</td>
<td>1,6-8, 10,12, 14,15, 17,20,21</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>WO 94 11569 A (MO OCH DOMSJŒ AB; LINDEBERG OTTO STEN AXEL GUSTA (SE)) 26 May 1994 (1994-05-26) * example 8 *</td>
<td>1,7-9, 12,14, 15,18-21</td>
<td>D21C</td>
</tr>
</tbody>
</table>

The present search report has been drawn up for all claims.

Place of search: MUNICH
Date of completion of the search: 13 November 2002
Examiner: Nestby, K

### CATEGORY OF CITED DOCUMENTS
- **X**: particularly relevant if taken alone
- **Y**: particularly relevant if combined with another document of the same category
- **A**: technological background
- **O**: written description
- **P**: intermediate document
- **D**: document cited in the application
- **T**: theory or principle underlying the invention
- **E**: earlier patent document, but published on, or after the filing date
- **L**: document cited for other reasons
- **A**: member of the same patent family, corresponding document
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int.Cl.)</th>
</tr>
</thead>
</table>

The present search report has been drawn up for all claims

Place of search

MUNICH 13 November 2002

Date of completion of the search

Examiner

Nestby, K

CATEGORY OF CITED DOCUMENTS

T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons
A: technological background
O: non-written disclosure
P: intermediate document

&: member of the same patent family, corresponding document
## Documents Considered to Be Relevant

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>Classification of the application (Int.Cl.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 6 056 853 A (VINCENT ADAM HAYDEN ET AL) 2 May 2000 (2000-05-02) * column 1, line 46 - column 1, line 51; claims 1,9 * -----</td>
<td>1,3-5, 7-9,12, 14,15, 18,19</td>
<td></td>
</tr>
</tbody>
</table>

The present search report has been drawn up for all claims.

Place of search: MUNICH
Date of completion of the search: 13 November 2002
Examiner: Nestby, K
# ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO. EP 02 01 3497

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EPO file on the European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-11-2002

<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AT 97179 T</td>
<td>15-11-1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 5621790 A</td>
<td>07-02-1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BR 9002660 A</td>
<td>20-08-1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2017807 A1</td>
<td>06-12-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69004492 D1</td>
<td>16-12-1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69004492 T2</td>
<td>24-03-1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 402335 T1</td>
<td>09-04-1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DK 402335 T3</td>
<td>17-01-1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0402335 A2</td>
<td>12-12-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ES 2038097 T1</td>
<td>16-07-1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI 107546 B1</td>
<td>31-08-2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2843892 B2</td>
<td>06-01-1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 302791 A</td>
<td>05-02-1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LT 444 A ,B</td>
<td>25-11-1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LV 10517 A ,B</td>
<td>20-02-1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO 902479 A ,B,</td>
<td>07-12-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NZ 233884 A</td>
<td>29-01-1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PT 94287 A ,B</td>
<td>08-02-1991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 8902058 A</td>
<td>07-12-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RU 2026437 C1</td>
<td>09-01-1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 5310458 A</td>
<td>10-05-1994</td>
</tr>
</tbody>
</table>

|                                       |                 | AT 130888 T             | 15-12-1995      |
|                                       |                 | AU 641858 B2            | 30-09-1993      |
|                                       |                 | AU 1514892 A            | 11-03-1993      |
|                                       |                 | AU 4204393 A            | 21-10-1993      |
|                                       |                 | BR 9201553 A            | 01-12-1992      |
|                                       |                 | CA 2067295 A1           | 31-10-1992      |
|                                       |                 | CA 2102713 A1           | 31-10-1992      |
|                                       |                 | DE 69206313 D1          | 11-01-1996      |
|                                       |                 | DE 69206313 T2          | 18-04-1996      |
|                                       |                 | EP 0554965 A1           | 11-08-1993      |
|                                       |                 | ES 2080427 T3           | 01-02-1996      |
|                                       |                 | FI 921887 A             | 31-10-1992      |
|                                       |                 | FI 934833 A             | 01-11-1993      |
|                                       |                 | JP 2069315 C            | 10-07-1996      |
|                                       |                 | JP 5148785 A            | 15-06-1993      |
|                                       |                 | JP 7096756 B            | 18-10-1995      |
|                                       |                 | NO 921670 A ,B,         | 02-11-1992      |
|                                       |                 | NO 934006 A             | 02-11-1992      |
|                                       |                 | NZ 242466 A             | 26-08-1994      |
|                                       |                 | SE 9101300 A            | 31-10-1992      |

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82
This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-11-2002

<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP 0512590 A</td>
<td></td>
<td>RU 2071519 C1</td>
<td>10-01-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 5658429 A</td>
<td>19-08-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZA 9203074 A</td>
<td>30-12-1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AT 193912 T</td>
<td>15-06-2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BR 9611974 A</td>
<td>03-11-1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2239876 A1</td>
<td>31-07-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 1203643 A</td>
<td>30-12-1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69608910 D1</td>
<td>20-07-2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69608910 T2</td>
<td>18-01-2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 08666895 A2</td>
<td>30-09-1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 9727358 A2</td>
<td>31-07-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZA 9610276 A</td>
<td>30-07-1997</td>
</tr>
<tr>
<td>US 4450044 A</td>
<td>22-05-1984</td>
<td>NO 781190 A</td>
<td>05-10-1979</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 1119360 A1</td>
<td>09-03-1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI 791056 A, B</td>
<td>05-10-1979</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 439508 B</td>
<td>17-06-1985</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 7902901 A</td>
<td>05-10-1979</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE 9203366 A</td>
<td>12-05-1994</td>
</tr>
<tr>
<td>US 6056853 A</td>
<td>02-05-2000</td>
<td>AT 197825 T</td>
<td>15-12-2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 695415 B2</td>
<td>13-08-1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 5991196 A</td>
<td>09-01-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69611091 D1</td>
<td>04-01-2001</td>
</tr>
</tbody>
</table>

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82