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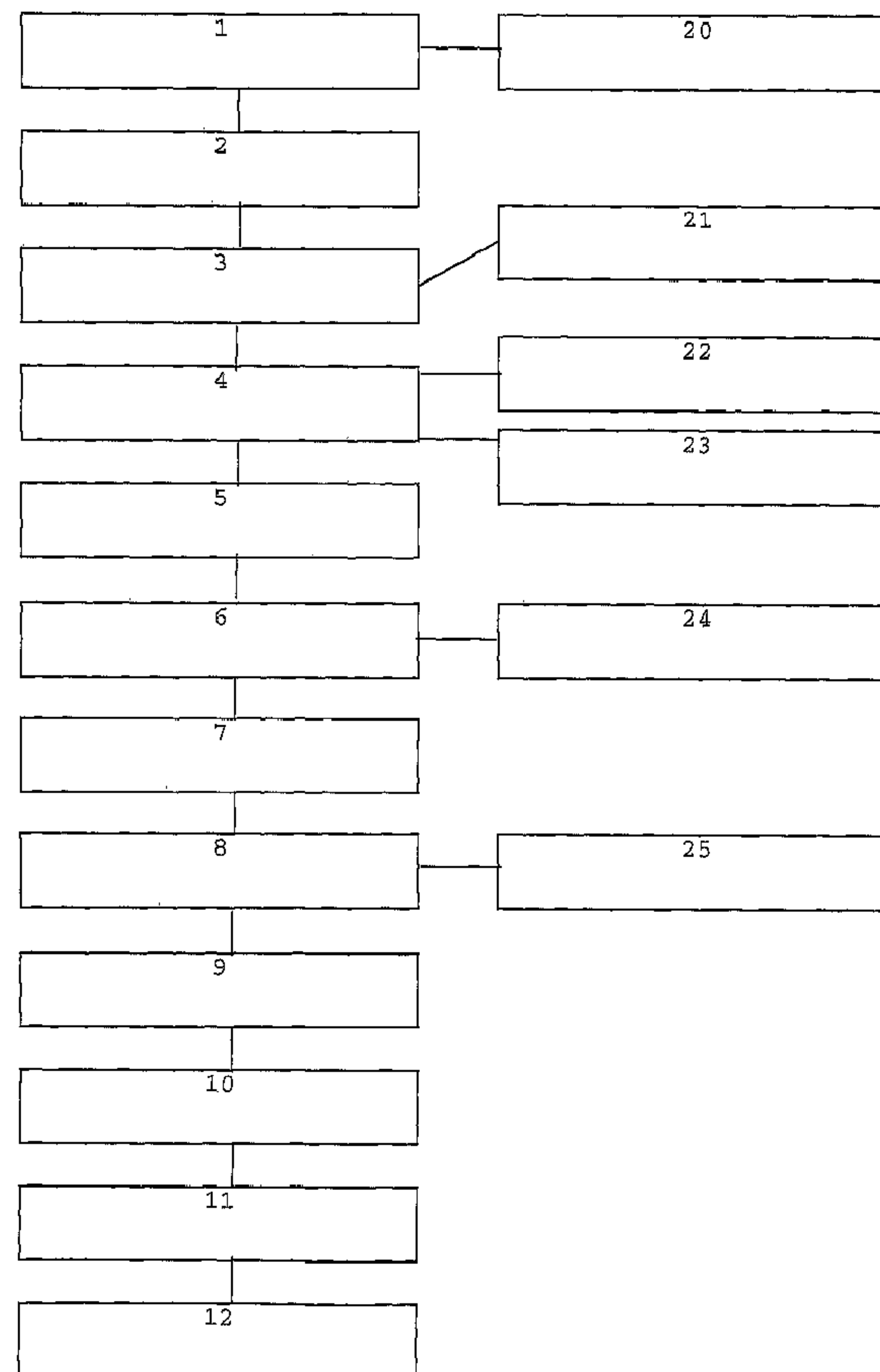
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(54) Titre : PROCÉDE POUR DECOLORER DES MATIERES FIBREUSES

(54) Title: METHOD FOR BLEACHING FIBROUS MATERIAL



(57) Abrégé/Abstract:

The invention relates to a method for bleaching fibrous materials, in particular lignin-containing materials for producing paper consisting in adding at least a first additive and at least one type of bleaching liquid to a fibrous solution which contains at list one

(57) **Abrégé(suite)/Abstract(continued):**

bleaching agent. After mixing said bleaching solution with the fibrous suspension and at the end of determined bleaching time, the bleaching process is ended by adding at least a second additive. Said invention is characterised in that the pH of the fibrous suspension is obtained by adding lime.

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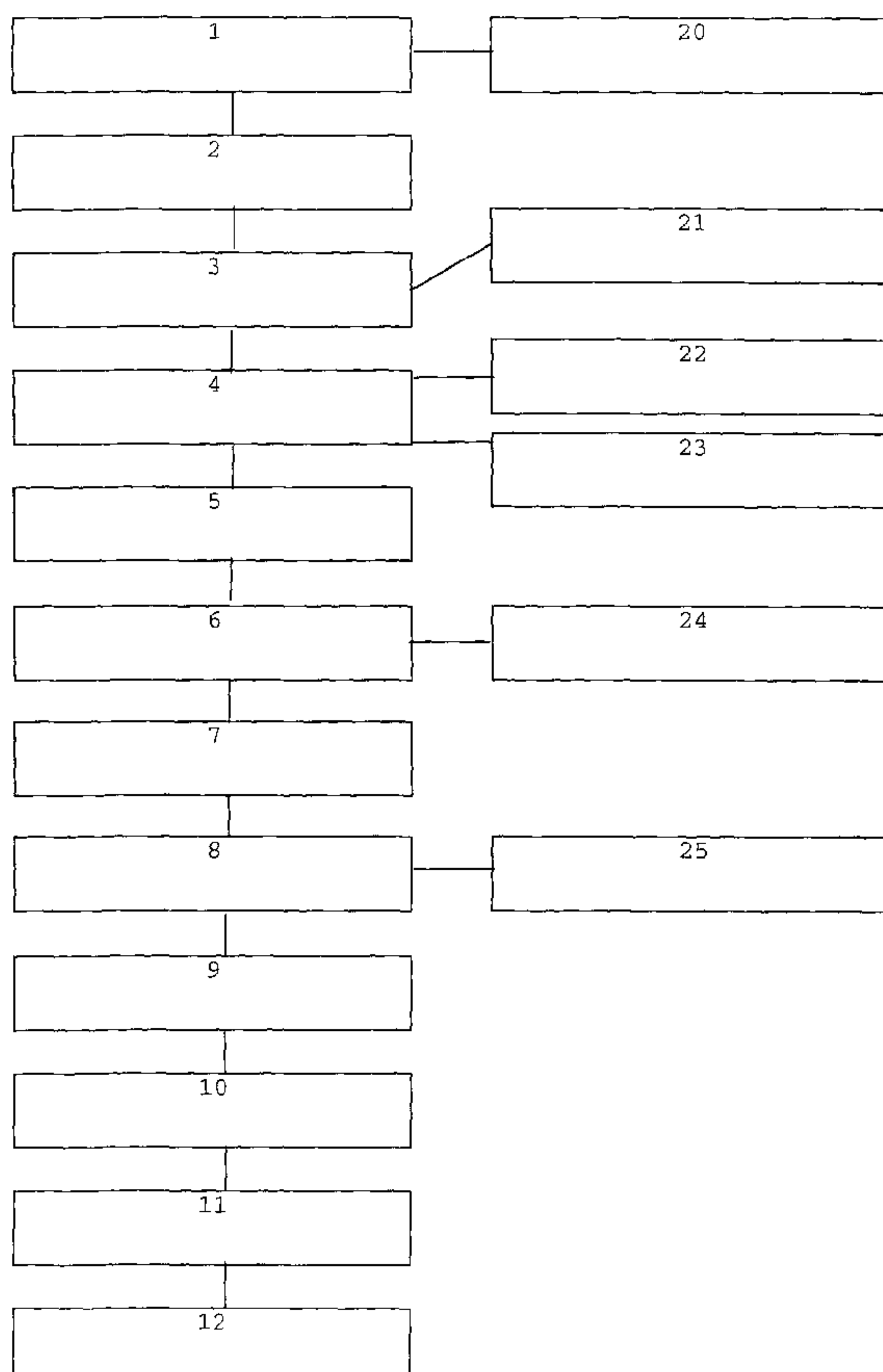
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(54) Title: METHOD FOR BLEACHING FIBROUS MATERIALS

(54) Bezeichnung: VERFAHREN ZUM BLEICHEN VON FASERSTOFFEN



(57) **Abstract:** The invention relates to a method for bleaching fibrous materials, in particular lignin-containing materials for producing paper consisting in adding at least a first additive and at least one type of bleaching liquid to a fibrous solution which contains at list one bleaching agent. After mixing said bleaching solution with the fibrous suspension and at the end of determined bleaching time, the bleaching process is ended by adding at least a second additive. Said invention is characterised in that the pH of the fibrous suspension is obtained by adding lime.

(57) **Zusammenfassung:** Die Erfindung betrifft ein Verfahren zum Bleichen von Faserstoffen, insbesondere von ligninhaltigen Faserstoffen für die Herstellung von Papier. Das Verfahren beinhaltet die Zugabe von wenigstens einem ersten Additiv und wenigstens einer Bleichlauge in die Faserstoffsuspension, wobei die Bleichlauge wenigstens ein Bleichagens aufweist. Nach dem Vermischen der Bleichlauge mit der Faserstoffsuspension und nach einer vorgegebenen Bleichdauer wird der Bleichprozess durch die Zugabe von wenigstens einem zweiten Additiv beendet. Das Verfahren ist ferner dadurch gekennzeichnet, dass die pH-Werteinstellung der Faserstoffsuspension durch die Zugabe von Kalk erfolgt.

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Method for bleaching fibrous material

The present invention relates to a method and a device for bleaching fibre materials, in particular lignin-containing fibre materials for the production of paper.

Methods for bleaching fibre materials are known in the state of the art, wherein, in addition to oxidative bleaching means, reductive bleaching means are also used in the paper industry for bleaching fibre materials.

In industry, bleaching of lignin-containing fibre materials is carried out in particular using lignin-preserving bleaching sequences, which are presently, particularly for reasons of environmental protection, halogen-free bleaching sequences using for example hydrogen peroxide, oxygen or ozone as bleaching means.

For attaining an optimal bleaching result, besides the application of a specific bleaching means, the process control, in particular the process conditions, is also of decisive significance.

Thus, for example, sodium hydroxide is used in conjunction with the application of hydrogen peroxide, which is admixed to the fibre material in form of caustic soda lye (aqueous sodium hydroxide solution) together with the hydrogen peroxide, or before the hydrogen peroxide is added.

The disadvantages of using caustic soda lye are its relatively high cost and the problems associated with its dosage. Thus, in particular a large deviation of the pH value as a result of using caustic soda lye will lead again to a reduction of the initial degree of whiteness of the fibre material to be bleached.

It is the object of the present invention to overcome the known disadvantages of the prior art at least partially and, in particular, to provide a cost effective method featuring the use of a cheap lye for bleaching fibre materials for the paper industry.

According to the present invention, the method for bleaching fibre materials, in particular of lignin-containing materials for the production of paper, includes a plurality of steps, where in at least one of those steps at least one first additive is dosed into a suspension of fibre material.

According to the present invention, there is provided a method for bleaching fibre materials, in particular lignin-containing fibre materials for the production of paper, comprising

- adding at least one first additive into a suspension of fibre material;
- adding at least one bleaching lye into the suspension of fibre material, the bleaching lye having at least one bleaching agent;
- mixing the bleaching lye with the suspension of fibre material;
- completing the bleaching process with the addition of at least one second additive,

characterized in that lime is used at least for adjusting the pH value of the suspension of fibre material before the bleaching.

According to the present invention, there is provided a method for bleaching lignin-containing fibre materials for the production of paper, the method comprising :

adding, into a suspension of fibre material, at least one first additive for bleaching, at least one bleaching lye including at least hydrogen peroxide as a bleaching agent, and mixing the bleaching lye with the suspension of fibre material,

characterized in that :

bleaching is terminated by the addition of at least one reductive agent to the bleaching agent,

0.01 % to 5 % by weight of lime, based on the oven-dry weight of fibre material, is used at least for adjusting the pH value of the suspension of fibre material between 8 and 12 before bleaching,

material density of the suspension of fibre material is between 5 % and 55 %.

According to the present invention, there is provided a device for bleaching fibre materials with at least one mixer and one reaction space in which an aqueous

suspension of fibre material is subjected to at least one bleaching, in particular one bleaching stage,

characterized in that

a dosing device, which regulates and/or controls the addition of lime, in particular a lime at least partially dispersed in water, into the aqueous suspension of fibre material in the bleaching process as a function of predefined process parameters is provided.

According to the present invention, a suspension of fibre material is understood to be an aqueous suspension of fibre material containing in particular natural fibres such as cellulose, waste paper, mechanical wood pulp and suchlike. Besides the fibre materials, the suspension can however also include mineral or other types of components, as is the case particularly when waste paper is used as heterogeneous raw material.

Besides the addition of the first additive, at least a bleaching lye is dosed to the fibre material, in particular into the suspension of fibre material, the bleaching lye including at least one bleaching agent. According to the invention, both the first additive and the bleaching lye are mixed with the suspension of fibre material, the bleaching process then finalizing, according to the invention, with the addition of at least one second additive.

According to the present invention, the pH value of the suspension of fibre material is adjusted using lime that is, according to a particularly preferred embodiment of the invention, dispersed at least partially in water.

According to the present invention, the pH value adjustment is carried out by means of the dosed addition of lime in such a manner that either the amount of lime is dosed as a function of a pH value determined in the suspension of fibre material and/or, according to a particularly preferred embodiment, the dosage is conducted as a function of the amount of bleaching lye used. However, other dosage forms are also imaginable, such as, for example, dosing as a function of the amount of fibre material and/or suchlike, which are also understood to be dosing methods according to the present invention.

According to the present invention, lime is understood to be a substance including at least one component being selected from a group including calcium hydroxide,

calcium oxide, (calcium) carbonate, fired natural and/or synthetic minerals, such as, for example, orthoclase, albite, anorthite, kaolinite, mullite, muscovite, calcite, magnesite, artinite, periclase, brucite, dolomite, wollastonite, talc and clinochlore. Furthermore, this group can include further substances, which are preferably but not exclusively added as impurities and which are, for example, magnesium (oxide), aluminium silicates/oxides and/or transition metal components, in particular iron and manganese oxides/hydroxides, sodium oxide, potassium oxide, silicon oxide, sulfur oxide, as well as bound gaseous components and suchlike.

According to the present invention, mechanical wood pulp is understood to be, in particular, stone groundwood with and without chemical pretreatment, refiner mechanical pulp with and without chemical pretreatment, thermo-mechanical pulp, reground stone groundwood pulp, pressurized stone groundwood, refiner mechanical pulp, pressurized refiner mechanical pulp, chemi-groundwood, chemi-refiner mechanical pulp, chemi-thermo-mechanical pulp and suchlike.

According to a particularly preferred embodiment, the method according to the present invention is used for bleaching fibre materials having a material density between 5 % and 55 %, preferably between 10 % and 50 %, particularly preferably between 15 % and 46 %. In this context, the material density can be between 5 % and 20 % for so-called low consistency, between 20 % and 28 % for a medium consistency, and between 28 % and 46 % for a so-called high consistency.

According to a further preferred embodiment, the material density is reduced by adding process water and/or fresh water.

According to a further particularly preferred method, the material density of the fibre material is increased mechanically and/or thermally and/or chemically, that is to say that liquid is removed from the dispersion. In particular, the mechanical increase of the material density is carried out, for example, through the removal of water from the suspension of fibre material by means of a twin wire press, a disc filter or suchlike, as they are known in the state of the art.

According to the present invention, the chemical increase of the material density is understood to be the addition of dry components, such as lime, which has not been dispersed in water at least partially in a preceding dispersion step, but is, instead,

dosed into the suspension of fibre material as a solid, thereby increasing the material density of the suspension of fibre material, that is to say, the solid content in relation to a predefined volume.

According to a preferred embodiment, the bleaching lye being dosed into the suspension of fibre material contains at least one substance with oxidative or reductive effects, causing at least partial bleaching of the fibre material, in particular the at least partial destruction of chromophoric groups, as known in the state of the art. According to a particularly preferred embodiment, these agents are selected from within a group containing hydrogen peroxide, hypochloride, ozone, oxygen, sodium sulfite, formamidine sulfonic acid, sodium dithionite, sodium borohydride, peracetic acid, perchloric acid, hydrosulfite, and suchlike.

It should be noted, however, that in the case of fibres, which are in particular loaded with impurities with only very weak or no catalytic effect, the addition of substances such as complexing agents can be dispensed with. The same applies to the use of water glass, such as alkaline silicates and alkaline earth silicates.

According to a particularly preferred embodiment of the present invention, the first additive is understood to be an auxiliary means selected from a group containing water glass, in particular alkaline and/or alkaline earth silicates, complexing agents such as DTPA, EDTA and phosphates and phosphonates, polyhydroxycarboxylic acids, sugar derivatives, stabilizers, catalysts, inhibitors and suchlike.

According to a further embodiment of the present invention, agents complementing the bleaching lye are used as the second additive, whereby, according to another particularly preferred method, the agents are selected from a group containing reductive and oxidative agents, such as hydrosulfite, sodium bisulfite, sodium hydrosulfite, sodium borohydride and suchlike.

According to a preferred executive example, they are used, amongst other things, to reduce residues of the bleaching agent previously added by means of the bleaching lye as much as possible at the end of the bleaching process, so that its effectiveness for a further subsequent treatment may not adversely affect the use of further bleaching agents, for example in a second step. According to a particularly preferred embodiment, these can be different bleaching agents, although it is also possible to

achieve the desired effect in a single step by means of a selective agent.

According to a further particularly preferred method, the lime is stored as a solid and is taken out essentially continuously from a container. Here, essentially continuously is understood to mean a pulsed extraction, as well as a continuous extraction, with and without interruptions, and combinations thereof. The speed of extraction must also not be constant, but can instead be regulated and/or controlled according to the predefined dosage.

According to a further preferred method, the lime has a solids content of between 92 % and 100 %, preferably of between 95 % and 99.9 %, and particularly preferably of between 98 % and 99.5 %.

During the dosage of the lime dissolved and/or dispersed in water, i.e. the dosage of the lime milk into the fibre material suspension, the latter has a solids content of between 5 % and 40 %, preferably of between 7 % and 25 % and particularly preferably of between 10 % and 20 % and particularly of less than 17 %.

The determination of the solids contents is carried out in accordance with the regulations set forth by the German Industrial Standard, for example DIN ISO 787, part 2, or the TAPPI standards known in the state of the art. The equivalent applies to the determination of further characteristics, which are known in the state of the art as process parameters, quality properties and suchlike within the context of pulp and paper production, and which can be obtained from the DIN or TAPPI standards.

As already explained, the lime can be also be dosed to the fibre material as a solid, whereat, according to a particularly preferred method, the lime has a predefined particle size distribution.

The lime dosage can take place before the addition of the first additive and bleaching lye into the suspension of fibre material, the addition of the lime also being possible after the addition of the first additive and before the addition of the bleaching lye. According to a further particularly preferred embodiment, the lime can also be dosed into the suspension of fibre material essentially simultaneously with at least one first additive.

According to the present invention, after the dosage of the lime into the suspension of

fibre material, a pH value in the suspension of fibre material ranging between 8 and 12, preferably between 9 and 11 and particularly preferable between 10.3 and 10.8 is attained.

Furthermore, the amount of lime added in relation to the oven dried (odri) amount of fibre material can be between 0.01 % and 5 %, preferably between 0.1 % and 2 %, and particularly preferably between 0.3 % and 1 %. In addition, a dosage dependent on the amount of the bleaching means is provided according to a further executive example, a hydrogen peroxide to lime ratio of between 0.1 and 5, preferably of between 1 and 3 and particularly preferably between 2.4 and 2.7 being selected.

According to a further particularly preferred executive example, the fibre material is heated by means of steam addition, in particular of low pressure steam and/or by the introduction of mechanical energy, such as is the case, for example, when mixing in a high consistency mixer, to a temperature between 40°C and 100°C, preferably between 45°C and 90°C and particularly preferably between 60°C and 70°C.

The addition of the second additive can take place, according to a further preferred method, after the dilution of the fibre material, being given that sufficient mixing must be ensured in this case as well.

According to a further preferred executive example, process water is used for the dilution of the fibre material, process water being understood to be production water created within the area of fibre material bleaching, paper production or equivalent process stages.

According to another particularly preferred embodiment of the method for bleaching fibre materials, a complexing agent is dosed to the fibre material, in particular into the suspension of fibre material, the complexing agent particularly reducing the catalytic effect of metals such as transition metals, in particular metal ions, on the decomposition of at least one bleaching agent. Diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), phosphates, phosphonates, polycarboxylic acids, sugar derivatives, polyhydroxycarboxylic acids and suchlike can for example be used as complexing agents.

The object is also solved by a device for bleaching fibre materials, including at least

one mixer and one reaction space, in which the aqueous suspension of fibre material is subjected to at least one bleaching, in particular bleaching stage, according to predefined conditions.

This device is further characterized in that a dosing device, which regulates and/or controls the addition of lime, in particular a lime at least partially dispersed in water, into the aqueous suspension of fibre material as a function of predefined process parameters is provided.

According to a particularly preferred embodiment of the device according to the invention, the process parameters are selected from a group of parameters containing the pH value, the amount of bleaching agent, the amount of bleaching lye, the brightening, the degree of whiteness, the chromaticity coordinate, the reaction time, the bleaching temperature, the content of residual bleaching means, the amount of fibre material, the solids content, the material density, the pressure, the mixing and suchlike.

According to another preferred executive example of the device, the lime is taken out essentially continuously from a storage container, preferably as a solid, and diluted with water to a predefined solids content before being added into the suspension of fibre material. In particular fresh water such as well and/or surface water and/or process water can be used as possible diluting water.

The object is further solved by a device for bleaching fibre materials, including at least a first container for storing lime having a predefined particle size distribution and purity, an extracting device and a transport and/or mixing device, in which the lime is dissolved and/or dispersed, and further including at least a second container, to which the lime is transported and in which the latter is mixed with a suspension of fibre material according to predefined process parameters.

Further explanations are provided hereinafter with reference to the figures and the executive example. The results shown here shall however not limit the scope of the invention and merely represent executive examples aimed in particular at the application of the system for bleaching mechanical wood pulp. It is however also possible within the meaning of the present invention to use the present method or, alternatively the device according to the present invention, for other fibre materials, as

was explained earlier.

Accordingly:

Fig. 1 shows a flow diagram for the implementation of the method for bleaching fibre materials according to the invention.

Fig. 1 represents a schematic flow diagram for the implementation of the method for bleaching lignin-containing mechanical wood pulps, such as those used for example for the manufacture of stone groundwood for the production of paper, in particular mass-print papers.

Before the actual bleaching, the fibre material is taken out from a storage container 1, the so-called storage tower, the transport being facilitated by diluting the wood pulp through the addition of process water 20, for example filtrate, and feeding it to a mechanical thickening device 2 by means of a feed system.

The thickening device 2 can be, for example, a twin wire press, which increases the material density of the mechanical wood pulp to a range of between 25 % and 28 % solids content.

Other water removal techniques known in the state of the art are however also possible.

According to a particularly preferred embodiment, the fibre material can already have a first additive, such as a complexing agent, dosed to it in the storage container, at its outlet, or in the transport device, the dosing amount being dependent in particular on the loading of the fibre material or dilution water with possibly catalytically acting metals, in particular metal ions. According to the executive example presented here, 0.3 % of DTPA per 9 t of wood pulp are added to the wood pulp.

The thickened fibre material is transported from the twin wire press 2 over a feed screw 3 and a transport device to a mixing device 4.

According to the embodiment presented here, the lime 21 is dosed to the fibre material already at the feed screw 3, the feed screw 3, in particular, being used for mixing of the fibre material with the lime milk 22. The fibre material is subsequently

shredded, loosened and transported. It is, however, also compatible with the meaning of the present invention to place the dosing location in another position, in particular when the reaction time and the mixing are adapted to the predefined conditions.

To ensure sufficient mixing and homogenization of the fibre material, according to a particularly preferred embodiment, an exposure time is selected between the addition of the lime milk 22 and the following dosage of further additives or bleaching agents 23, depending on the position of the dosing location and taking into consideration the flow conditions.

According to the executive example presented here, the exposure time is preferably between 10 and 60 seconds.

The mixing of the fibre material after the dosed addition of a further additive, for example an alkaline or alkaline earth silicate, and the dosed addition of the bleaching lye, in particular of the bleaching agent, takes place according to the method presented here by means of a high consistency mixer 4. The material density is between 18 % and 35 %, being given that, according to the executive example presented here, a so-called high consistency mixer (Kamyr mixer), as known in the state of the art, is used. Other mixing devices can, however, be used as well, such as, particularly, but not exclusively, a double shaft mixer, particularly when the material density of the fibre material is adjusted within the low and medium concentration range.

Subsequent to the mixer, the fibre material is conveyed by means of a transport device, such as, for example, a feed screw 5 for a material density > 20 %, into a reaction space 6 such as, for example, a bleaching tower.

It should be noted, however, that the tests were carried out at the above-mentioned material density. It is however explicitly within the meaning of the present invention not to limit the material density to this value for the implementation of the method, but rather to consider a wide range of adjustment for the material density of the fibre material.

According to the executive example presented here, the fibre material is heated to a predefined temperature by supplying mechanical energy in the high consistency mixer

and/or through the addition of low pressure steam. According to the executive example presented here, this temperature lies in the range between 55°C and 70°C, although it should be noted that exceeding a temperature of 80°C is detrimental, particularly when using alkaline and/or alkaline earth silicates, because at this temperature a precipitation of the additives can already take place, e.g. through the formation of quartz sand.

It should further be noted that observance of the above-mentioned temperature limits for the bleaching process is not required when the use of such auxiliary means is dispensed with, so that the temperatures predefined by the system can be used in full and, for example, exceed 90°C.

To ensure that sufficient time is available for the bleaching agent to react with the fibre material, in particular with the chromophoric groups of the fibre material, the residence time of the fibre material with the added bleaching agent 23 and lime milk 22 inside the bleaching tower is 30 to 180 minutes, with the reaction time being determined in particular as a function of the desired degree of whiteness and/or residual content of bleaching agent in the fibre material.

According to the executive example presented here, the reaction time is between 60 minutes and 3 hours for a material density of approximately 20 % to 27 % and a temperature of between 60°C and 70°C. The pH value in the initial stage is approximately 10.8 % to 11.2 % and falls to a value of between 6.3 % and 7.3 % in the course of the bleaching stage.

According to the executive example presented here, the fibre material is diluted with process water 24 after an extracting location, the material density then being between 2 and 5 % according to the executive example presented here.

It should further be noted that, before and/or after the dilution with process water, a second additive is added to the fibre material taken out from the bleaching tower 6, which, according to the executive example presented here, reduces the amount of residual bleaching agent possibly still present within the fibre material in such manner as to conclude the bleaching stage.

This fibre material is fed by means of a transport device to a further mechanical water

removal device 7 - e.g. a twin wire press -, in which the material density is increased to a range of between 18 % and 35 %, particularly to 26 %. The fibre material is accumulated in the feed screw 8 according to the example presented here and fed into a storage vat 9.

According to a particularly preferred executive example, the fibre material has its degree of whiteness further increased and/or its chromaticity coordinate changed in a subsequent second stage by means of the application of a further, in particular reductive bleaching agent 25. This bleaching can again take place, for example, in a reaction container, e.g. a bleaching tower 10, with the reaction time essentially here also depending on the agent used. The then completely bleached mechanical wood pulp is intermediately stored in a so-called storage vat 11 for processing in the production of paper 12.

Application example:

The executive example shown hereinafter illustrates four practical bleaching tests using mechanical wood pulp which was bleached with the method according to the present invention.

Here, the three tests differentiate themselves amongst other things in the amount of active bleaching agent used, here hydrogen peroxide (H_2O_2), and in the amount of added lime or water glass. The exact amounts used can be obtained from Table 1: Amounts used.

Table 1: Amounts used

	Test 1	Test 2	Test 3	Test 4
H_2O_2 [50 %]	3.0 %	6.0 %	7.4 %	3.0 %
Lime [17 %]	2.2 %	3.4 %	3.8 %	2.2 %
Water glass	0.9 %	2.2 %	3.0 %	0.9 %
Mixing unit	High consistency mixer	Double shaft mixer	High consistency mixer	High consistency mixer
Material density	26 %	20 - 25 %	26 %	~17.5 %
Temperature	65 °C	~ 55 °C	65°C	65°C

A high consistency mixer (Kamyr mixer) was used as the mixing unit in test series 1, 3 and 4 and a double shaft mixer was used as the mixing unit in test series 2.

The material density in test series 1 and 2 was 26 %, in test series 2 it was 20 to 25 %, and in test series 4 it was approximately 17.5 %. The reaction temperature was set at 65°C for test 1 and was at approximately 55°C for test 2.

While performing these tests, quick lime (calcium hydroxide; $\text{Ca}(\text{OH})_2$) with a certain fraction of impurities was used as lime or lime milk. The lime was stored in a silo as a solid and diluted to a solids content of approximately 17 % with fresh water by means of an extracting device and a dispersion device connected thereto.

The bulk density of the lime was 0.5 g/cm^3 , (EP 459-2), with the sieve analysis according to EP 459-2 resulting in a 0.0 % residue for a 0.2 mm sieve and a 2.1 % residue for a 0.09 sieve.

The amounts used according to the formulation relate explicitly to the amount of oven dried wood pulp introduced. The process control corresponds to the flow diagram represented in figure 1.

The test results can be obtained from Table 2.

Table 2: Measured values

	Test 1	Test 2	Test 3	Test 4
Initial whiteness (R457)	~ 62	~ 62	~ 62	~ 62
Final whiteness (R457)	~ 74	~ 76,5	~ 78,5	~ 74
COD value	< 1700	~ 2500	< 1700	~ 1650
Residual peroxide	20 - 300 20 - 150	300 - 600	20 - 300	20 - 150
CaO value	150 - 250	150 - 300	25 - 400	150 - 250

(Percentages refer to odri fibre material)

Comparative values when using NaOH:

Hydrogen peroxide	(H ₂ O ₂)
[50 %]:	7.4
NaOH [50 %]:	4.0
Water glass:	1.7
Residual peroxide:	90 - 800 or 200 - 350
CaO value:	85 - 120
COD value:	Bleaching tower 1B >2800; Bleaching tower 1A 4000 - 5000

Apart from the final whiteness obtained, the measured COD values, residual peroxide contents and calcium oxide values are particularly notable.

Compared to the results obtained when using caustic soda lye, the COD value of < 1700 falls clearly below the value obtained with the application of caustic soda lye. In practical tests, this tendency also affected the COD load in the inlet and outlet of the final clarification of the wastewater treatment plant connected to the factory. Here, the COD load in the inlet was reduced by about 15 % for full capacity operation of a bleaching line. A COD reduction of 25 % is realistic if all the bleaching lines are operated with lime milk.

The residual peroxide content, which expresses the bleaching effect of the peroxide on the fibre material, was clearly lower compared to the results obtained when using caustic soda lye, with the determined values lying between 20 and 300 or between 20 and 150. The measurement took place in the individual fibre material filtrate prior to the dilution preceding the bleaching in the reaction space.

Solely the value for the amount of calcium oxide in the bleached fibre material increased slightly when using lime milk in comparison to the application of caustic soda lye, with the values in the range of 150 to 250 being within the process tolerance limits.

It should further be noted that, on the basis of practical tests and the associated quality criteria for the application of the bleached mechanical wood pulp in production, the degree of whiteness in tests 1 and 2 was used as control quantity for the

application of hydrogen peroxide.

In addition to the above-mentioned test results it should further be recorded that with the application of the so-called "lime milk" a more stable bleaching process, which is also reflected by a more stable degree of whiteness was achieved. This way, the fluctuations relating to the application of caustic soda lye were typically between 2 and 5 degrees of whiteness, while for the application of lime milk the fluctuations were at < 1.5 degrees of whiteness. Generally, the tolerance for dosing errors was noteworthy with lime milk. Among other things, an overdosing of 20 % lime milk did essentially not have a negative influence on the final whiteness.

Temporary increases of the degree of whiteness above average were also registered with the application of lime milk.

The use of lime as a bleaching agent is also interesting from an economical point of view. Thus, the price level for slaked lime as a product for processing a raw material available in nature is well below that of caustic soda lye, which is produced in a complex process by means of chlor-alkali electrolysis. Furthermore, it is much less volatile. In addition, it should be noted that the actual required amount of bleaching agent can be partly noticeably reduced.

Claims

1. A method for bleaching lignin-containing fibre materials for the production of paper, said method comprising :

adding, into a suspension of fibre material, at least one first additive for bleaching, at least one bleaching lye including at least hydrogen peroxide as a bleaching agent, and mixing the bleaching lye with the suspension of fibre material,

characterized in that :

bleaching is terminated by the addition of at least one reductive agent to the bleaching agent;

0.01 % to 5 % by weight of lime, based on the oven-dry weight of fibre material, is used at least for adjusting the pH value of the suspension of fibre material between 8 and 12 before bleaching; and

material density of the suspension of fibre material is between 5 % and 55 %.

2. The method of claim 1, characterized in that the lime is dispersed at least partially in water.

3. The method of claim 1 or 2, characterized in that the lime has at least one component chosen from calcium hydroxide, calcium oxide, carbonates, natural and fired natural minerals, accompanying substances, and bound gaseous components.

4. The method of claim 3, characterized in that the natural and fired natural minerals are chosen from orthoclase, albite, anorthite, kaolinite, mullite, muscovite, calcite, magnesite, artinite, periclase, brucite, dolomite, wollastonite, talc and clinocllore.

5. The method of claim 3, characterized in that the accompanying substances are chosen from magnesium oxide, aluminium oxide, iron oxide, sodium oxide, potassium oxide, silicon oxide and sulfur oxide.
- 5 6. The method of any one of claims 1 to 5, characterized in that the fibre material is selected from a group of fibre materials containing natural fibre materials.
7. The method of any one of claims 1 to 5, characterized in that the fiber material is chosen from cellulose, waste paper, mechanical wood pulp, refiner mechanical pulp with and without chemical pretreatment, thermo-mechanical pulp, reground stone groundwood pulp, pressurized stone groundwood, refiner mechanical pulp, pressurized refiner mechanical pulp, chemi-groundwood, 10 chemi-refiner mechanical pulp and chemi-thermo- mechanical pulp.
8. The method of claim 7, characterized in that mechanical wood pulp is stone groundwood with and without chemical pretreatment.
9. The method of any one of claims 1 to 8, characterized in that the material 15 density of the suspension of fibre material is between 10 % and 50 %.
10. The method of any one of claims 1 to 8, characterized in that the material density of the suspension fiber material is between 15 % and 46%.
11. The method of any one of claims 1 to 8, characterized in that the material density of the suspension fiber material is between 5 % and 20 %.
- 20 12. The method of any one of claims 1 to 8, characterized in that the material density of the suspension fiber material is between 20 % and 28 %.
13. The method of any one of claims 1 to 8, characterized in that the material density of the suspension fiber material is between 28 % and 46 %.
14. The method of any one of claims 1 to 13, characterized in that process water 25 or fresh water is used for reducing the material density.
15. The method of any one of claims 1 to 14, characterized in that the at least one first additive for bleaching is chosen from water glass, complexing agents phosphonates, sugar derivatives, polycarbonic acids, stabilizers, catalysts and inhibitors.

16. The method of any one of claims 1 to 14, characterized in that the at least one first additive for bleaching is chosen from alkaline and alkaline-earth silicates.
17. The method of any one of claims 1 to 14, characterized in that the at least one first additive for bleaching is chosen from diethylenetriaminepentaacetic acid and ethylenediaminetetraacetic acid.
18. The method of any one of claims 1 to 17, characterized in that the reductive agent added to the bleaching lye is chosen from hydrosulfite, sodium bisulfite, sodium hydrosulfite and sodium borohydride.
19. The method of any one of claims 1 to 18, characterized in that the lime is taken out as a solid from a container essentially continuously.
20. The method of any one of claims 1 to 18, characterized in that the lime is aqueous dissolved and/or dispersed lime having a solid content of between 5 % and 30 % oven-dry.
21. The method of claim 20, characterized in that the aqueous dissolved and/or dispersed lime has a solid content of between 7 % and 25 % oven-dry.
22. The method of claim 20, characterized in that the aqueous dissolved and/or dispersed lime has a solid content of between 15 % and 20 % oven-dry.
23. The method of claim 20, characterized in that the aqueous dissolved and/or dispersed lime has a solid content of 17 % oven-dry.
24. The method of any one of claims 1 to 23, characterized in that the lime is dosed into the fibre material as a solid with a predefined particle size distribution.
25. The method of any one of claims 1 to 24, characterized in that the lime is dosed into the suspension of fibre material before or after with the addition of the additive for bleaching and the bleaching lye.

26. The method of any one of claims 1 to 24, characterized in that the lime is dosed into the suspension of fibre material simultaneously with the addition of the additive for bleaching and the bleaching lye.
- 5 27. The method of any one of claims 1 to 26, characterized in that the pH value of the suspension of fibre material after the addition of the lime is between 9 and 11.
28. The method of claim 27, characterized in that the pH value of the suspension of fibre material after the addition of the lime is between 10.3 and 10.8.
- 10 29. The method of any one of claims 1 to 28, characterized in that the amount of lime added is between 0.1 % and 2 in relation to the oven-dry amount of fibre material.
30. The method of claim 29, characterized in that the amount of lime added is between 0.3 % and 1 % in relation to the oven-dry amount of fibre material.
- 15 31. The method of any one of claims 1 to 30, characterized in that the fibre material is heated by the addition of steam, and/or during mixing by mechanical energy, to a temperature of between 50°C and 100°C.
32. The method of claim 31, characterized in that the fibre material is heated to a temperature of between 55°C and 90°C.
- 20 33. The method of claim 31, characterized in that the fibre material is heated to a temperature of between 60°C and 70°C.
34. The method of any one of claims 1 to 33, characterized in that the fibre material is diluted before the addition of the reductive agent to the bleaching lye.
- 25 35. The method of any one of claims 1 to 34, characterized in that said at least one first additive for bleaching is added to said suspension of fibre material and then said at least one bleaching lye including at least hydrogen peroxide as a bleaching agent is added to the suspension of fibre material.

36. Use of a device for bleaching fibre material in a method according to any one of claims 1 to 35 with at least one mixer and one reaction space in which an aqueous suspension of fibre material is exposed to at least one fibre material bleaching under predefined conditions, means for adding at least one first additive for bleaching, means for adding at least one bleaching lye into the suspension of fibre material, wherein the bleaching lye includes at least hydrogen peroxide as a bleaching agent, characterized in that there are provided means for adding to the bleaching lye at least one reductive agent by means of which the bleaching is terminated, and a dosing device, wherein the dosing device regulates and/or controls the addition of lime into the aqueous suspension of fibre material at a material density between 5 % and 55 % in the bleaching process as a function of predefined process parameters.
37. The use of claim 36, characterized in that the process parameters are chosen from the pH value, the amount of bleaching agent, the amount of bleaching lye, the brightening, the degree of whiteness, the chromaticity coordinates, reaction time, material density, pressure, mixing, temperature and content of residual bleaching means.
38. The use of claim 36 or 37, characterized in that the lime is taken out as a solid essentially continuously from a storage container and diluted with water to a predefined solids content before being added into the suspension of fibre material.
39. A method for using a device for bleaching fibre material in a method according to any one of claims 1 to 35 with at least one mixer and one reaction space in which an aqueous suspension of fibre material is exposed to at least one fibre material bleaching under predefined conditions, means for adding at least one first additive for bleaching, means for adding at least one bleaching lye into the suspension of fibre material, wherein the bleaching lye includes at least hydrogen peroxide as a bleaching agent, characterized in that there are provided means for adding to the bleaching lye at least one reductive agent by means of which the bleaching is terminated, and a dosing device, wherein the dosing device regulates and/or controls the addition of lime into the aqueous suspension of fibre material the bleaching process as a function of predefined process parameters, and characterized in that the process parameters are

chosen from the pH value, the amount of bleaching agent, the amount of bleaching lye, the brightening, the degree of whiteness, the chromaticity coordinates, reaction time, material density, pressure, mixing, temperature and content of residual bleaching means.

- 5 40. A method for using a device for bleaching fibre material in a method according to any one of claims 1 to 35 with at least one mixer and one reaction space in which an aqueous suspension of fibre material is exposed to at least one fibre material bleaching under predefined conditions, means for adding at least one first additive for bleaching, means for adding at least one bleaching lye into the
10 suspension of fibre material, wherein the bleaching lye includes at least hydrogen peroxide as a bleaching agent, characterized in that there are provided means for adding to the bleaching lye at least one reductive agent by means of which the bleaching is terminated, and a dosing device, wherein the dosing device regulates and/or controls the addition of lime into the aqueous
15 suspension of fibre material the bleaching process as a function of predefined process parameters, and characterized in that the lime is taken out as a solid essentially continuously from a storage container and diluted with water to a predefined solids content before being added into the suspension of fibre material.

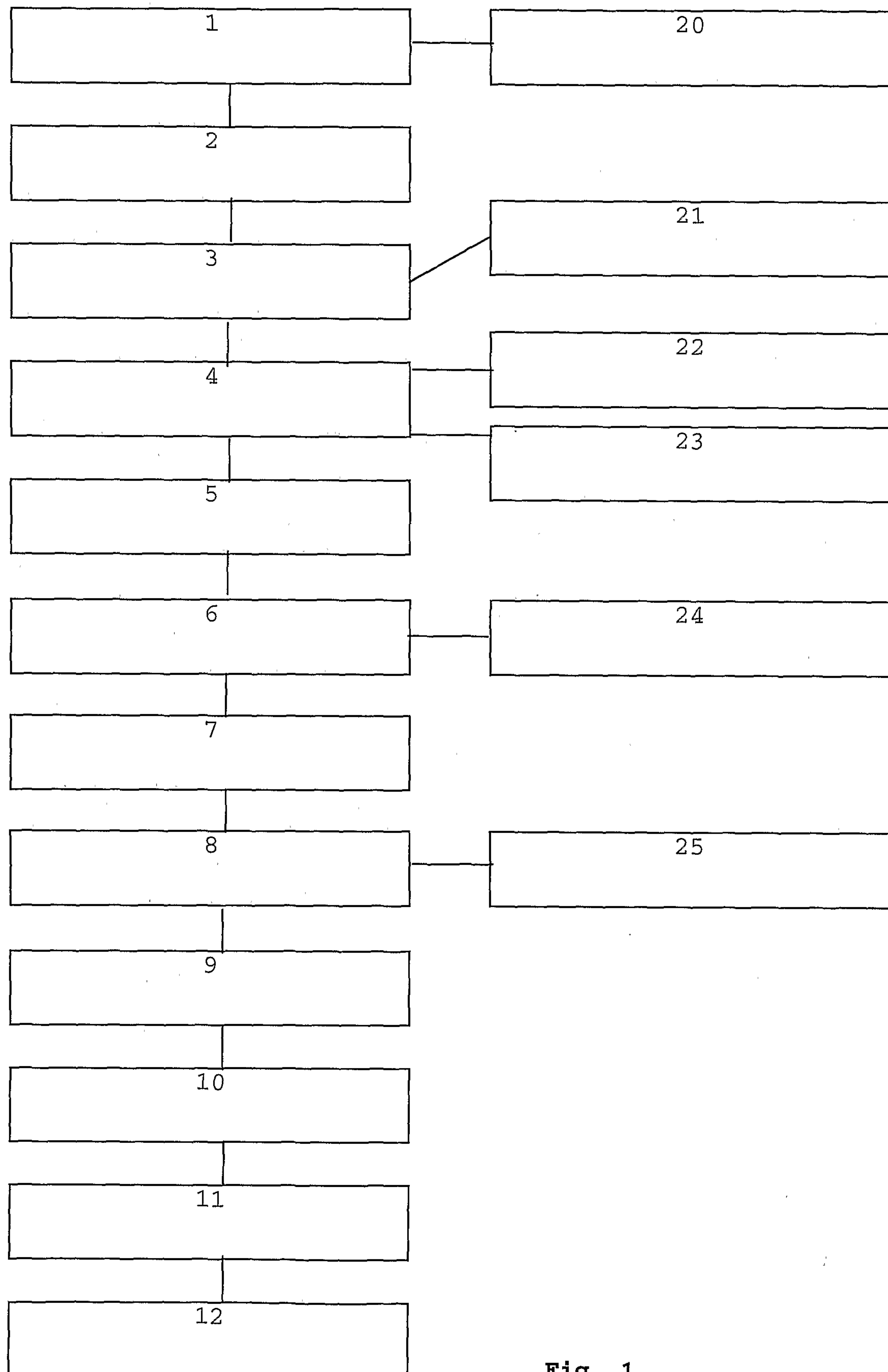


Fig. 1

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