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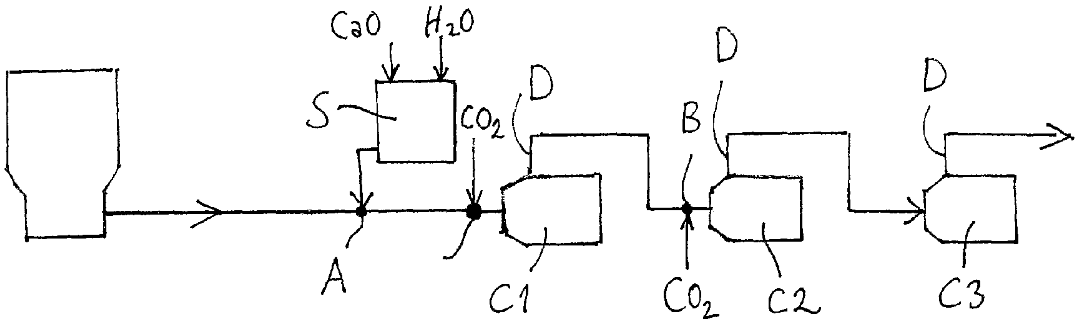
(54) **Title:** A METHOD AND A DEVICE FOR PRECIPITATING CALCIUM CARBONATE IN A FIBRE MATERIAL



(57) **Abstract:** In the method for precipitating calcium carbonate in the cellulose-based fibre material, the calcium compound is first directed to the fibre material, after which carbon dioxide is directed to this fibre material and the material is mixed in order to precipitate the calcium carbonate in the fibres. The carbon dioxide is directed to the fibre material, which is in a consistency of 3 to 5%, after which the fibre material is supplied in this consistency area through a mixing zone (Z) and brought on the mixing zone in question under hydraulic cutting forces in a defibrator (C; C1, C2), wherein the blade distance on said zone (Z) is in the area of 0.5 to 1.5 mm.

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A method and a device for precipitating calcium carbonate in a fibre material

The invention relates to a method for precipitating calcium carbonate in a fibre material, which is of the type presented in the preamble of the appended claim 1. The invention also relates to a device for implementing the method.

It is known to form calcium carbonate *in situ* in fibres by precipitating a calcium compound previously brought to the fibres by means of carbon dioxide. In precipitating calcium carbonate in fibres, the aim is for it to attach to the walls of the fibre used as the raw material in paper manufacturing and to fibre lumens in such a manner that an as good as possible loading is reached and the actual fillers do not need to be added separately in connection with paper manufacturing. Thus, the strength of the paper can be increased in comparison to paper that comprises the same amount of calcium carbonate filler as a separate addition. If a good loading of fibres is reached, i.e. the dry weight of calcium carbonate divided by the combined dry weight of calcium carbonate and fibres, the fibre with more expenses can be replaced significantly with calcium carbonate without having to decrease the strength of the paper.

The above-mentioned technique is described in several patent publications, of which can be mentioned, for example, US-patent 5,679,220. Here calcium hydroxide (lime milk) and carbon dioxide are directed sequentially to fibre slush, after which the precipitation of calcium carbonate takes place in a reaction zone, where the retention time is long enough in order to completely convert the calcium hydroxide. In the patent it is mentioned that the gaseous precipitant is brought to fast shearing when it is added to the fibre suspension. On lines 59 to 62 of column 7 of the patent, it is mentioned how more shearing can be developed with a pump, without, however, describing the arrangement more in detail. In the patent the use of a pipe-like reactor is introduced as an example. The recommended consistency of the fibre suspension is below 5 % according to this publication. According to US-patent 5,679,220, 10 to 75 % loadings with different fibres have been reached by means of the method and the retention of fillers in connection with paper manufacturing was 70 to 90 %.

In publication US-6,355,138 the precipitation of calcium carbonate takes place among the fibre suspension in a reactor, which is provided with a high consistency, 15 to 30 %, and the suspension is conveyed forward in the pipe-like reactor by means of a conveyor screw.

In a pipe reactor according to publication 5,679,220, it is difficult to reach a proper precipitation gas contact with the fibre suspension if the pipe reactor is dimensioned large in order to increase the capacity of production. Publication US-6,355,138 discloses a high consistency pulp method, which in turn requires proper mixing in order for the reactants to have a good enough contact with fibres.

Publication WO 02/072945 discloses a method wherein calcium hydroxide and/or calcium oxide are first supplied to the fibre suspension, and the thus processed suspension is compressed into a plug with a conveyor screw in a conically tapered channel, after which it is dispersed with a dispersing device between two discs located perpendicular in relation to the channel. One of the discs is fixed and one rotating. Carbon dioxide is supplied to the final end of the plug and/or to the input area of the dispersing device and/or to the central, radially inner area of the dispersing device. The dispersing device is at the same time used as a precipitation reactor for calcium carbonate. An advantageous decrease in the concentration of fibre suspension during the radial conveyance performed by the dispersing device is from 35 % to approximately 4 % according to the publication. This means that dilution water must be supplied to the dispersing device in order to reach this suitably low final consistency.

Thus in the solutions so far, in order to precipitate calcium carbonate into paper raw material fibre, reactors developed especially for that purpose have been used. Thus, the methods can be applied poorly into continuous manufacture of calcium carbonate containing pulp and, correspondingly, calcium carbonate containing paper in the pulp treatment lines used in factories.

The purpose of the invention is to overcome the above-mentioned drawbacks and to provide a new method for the continuous manufacture of calcium carbonate filled fibres for paper manufacturing. To attain this purpose, the method according to the invention is primarily characterized in what will be presented in the characterizing part of the appended claim 1.

Carbon dioxide is directed to cellulose-based fibres, to which calcium hydroxide has previously been impregnated, after which said fibres are processed in 3 to 5 % concentration in a defibrator, which can be a known processing device that disperses fibre bundles. In this kind of a defibrator there are grooves and ridges alternately in the rotation direction in the opposite surfaces, which rotate in relation to each other, i.e. blades between which the mixing zone for processing fibres is formed. In the suspension, the fibres in the mixing zone drift between opposite ridges and travel via larger spaces formed by opposite grooves, by being simultaneously exposed to hydraulic cutting forces. These cutting forces are enough to cause the calcium carbonate particles not to precipitate into fibres as too large particles, but as nano-sized particles.

In order to precipitate calcium carbonate, it is possible to use, for example, jumbo defibrators, or the like, free in the pulp manufacturing line. In this kind of a defibrator a blade gap in the mixing zone in question is in the range of 0.5 to 1.5 mm. In the defibrator the mixing zone forms a ring-like space expanding in its diameter in the supply direction of the fibre material.

In the following, the invention will be described in more detail with reference to the appended drawings, in which

Fig. 1 shows a continuous pulp processing line in a schematic view,

Fig. 2 shows a pulp treatment line according to a second embodiment,

Fig. 3 shows a pulp processing line according to a third embodiment, and

Fig. 4 shows a defibrator functioning as a precipitation reactor in a cross-section.

Fig. 1 shows a schematic view of a pulp processing line wherein the invention can be used. Lime milk (calcium hydroxide) is supplied continuously in the flow direction of pulp taken from a storage tank before the defibrator to the pulp flow in as high as possible dry solids content at point A, where the consistency of the pulp is between 3 to 5 %. Under the effect of the addition of calcium hydroxide, the pH of the pulp rises approximately to the value of 11 to 12. At the same time the pulp fibres swell. Lime milk is manufactured *in situ* without storage by continuously forming a slurry of calcium oxide in water. This is described with tank S in the graph of Fig. 1.

In the pulp flow direction, carbon dioxide is continuously added to the pulp flow after the lime milk addition point A at point B, which achieves the precipitation of calcium carbonate in fibres according to a known reaction. The addition of carbon dioxide at point B at the same time decreases the pH of pulp back to a normal level. Directly after point B, the pulp is supplied to the defibrator C, where the actual reaction takes place. The input of carbon dioxide takes place at a point where the consistency of pulp is 3 to 5 %, in which consistency the pulp is supplied to the defibrator. In the defibrator, where the consistency of pulp is still between 3 to 5 %, the fibre suspension is forced between the blades moving in relation to each other in such a manner that the fibres alternately drift between the ridges in opposite blades, and through these gaps have access to larger areas, which are in the grooves next to said ridges. The ridges are directed transversely in relation to the direction of rotation of the blades in order for the above-mentioned alternation to be possible during one cycle.

The processing in the above-mentioned manner can be implemented in known jumbo defibrators or the like, where the blades implementing the relative movement are formed of a rotor rotating around the axis and a fixed stator located coaxially in relation to this axis. The ring-like space between the blades and perpendicular to the rotation axis, which space has a certain tooth-like profile because of the above-mentioned ridges and which forms a mixing zone in order to get the fibre pulp impregnated with calcium hydroxide and carbon dioxide to react with each other, travels further from the rotation axis in the supply direction because of the conical form of the blades, i.e. its diameter widens and after travelling through this space the suspension, where the calcium carbonate has precipitated to the fibre walls and fibre lumens as nano-size particles (diameter typically below 0.1 μm), it ends in the discharge pipe D and travels along it further to the pulp processing system and the paper machine. The blade distance (the distance between the ridges of the opposite blades i.e. the rotor and the stator) is in this kind of defibrators typically at its minimum 0.5 mm, and the purpose of the defibrator is to disintegrate fibre knots (flocks) and not to refine fibres.

The carbon dioxide used, which is directed to the pulp flow, is advantageously 100 % gas.

An advantage in the use of the above-described defibrator is that while the fibre bundles are dispersed between the blades in a low consistency (3 to 5 %), the growth of the formed calcium carbonate into too large particles can be prevented. Thus, the calcium carbonate can remain attached to the fibre in small nano-size crystals with capillary forces and Van der Waals forces. The equivalent diameter (ESD) of the particles is advantageously between 40 to 100 nm.

Fig. 2 shows an advantageous manner to precipitate calcium carbonate in fibres. When lime milk has been added to pulp, the pulp can be directed in a consistency of 2 to 5 % to the first defibrator C1, before which the carbon dioxide is added to the pulp flow. After this defibrator and before the second defibrator C2, more carbon dioxide is added to the pulp flow. The first defibrator C1 and the second defibrator C2, which are connected in series, function as sequential precipitation reactors in order to precipitate nano-sized particles. In the end, the pulp flow coming out of the second defibrator can be processed in yet a third defibrator C3, where an effective mixing is achieved and it is ensured that all the fibres are processed.

It is advantageous to use at least two defibrators sequentially in series in such a manner that they are after at least one addition point of carbon dioxide. With this it is ensured that as many fibres as possible are in touch with carbon dioxide. Advantageously carbon dioxide is supplied in two sequential points before the corresponding defibrator.

In the pulp processing system of Fig. 3, lime milk can be added at point A to pulp flow, where the consistency is greater than in defibrator C. Between point A and the carbon dioxide addition point B, dilution into processing consistency of 3 to 5 % is performed for the pulp. The lime milk can be added, for example, into pulp travelling in a discharge screw of a disc filter F or other pulp concentrating device, the concentration of which pulp is over 10 %. In addition to the actual filtered suspension, auxiliary pulp also comes to the precipitating device, which also ends up in the discharge screw. After the discharge screw the pulp is directed to adilution tank T, where it is diluted to the processing consistency of 3 to 5 %, and after that to the carbon dioxide addition point B and the defibrator C. There can be defibrators C1 to C3 connected in series here as well.

Fig. 4 shows the defibrator C in a cross section. All the defibrators of Figs. 1 to 3 can be provided with this structure, especially those defibrators that are after the supply point of carbon dioxide. Fibre pulp is supplied to the defibrator in the direction of rotation of the rotor. The outer surface of the rotor and the inner surface of the stator are conical in their general form, and they form the above-mentioned processing zone Z between each other, which widens in its diameter in the supply direction, which zone is formed in a ring-like manner in the cross section plane perpendicular to the rotation axis of the rotor. The blade distance in zone Z is in the range of 0.5 to 1.5 mm. The zone Z can be formed of sequential subzones Z1, Z2 and Z3, through which the fibre material travels sequentially. The blade distances diminish stepwise in the supply direction in such a manner that in the first subzone Z1 the distance is 1.5 mm, in the second subzone Z2 1.0 mm and in the third subzone Z3 0.5 mm. As can be seen in the figure, the subzones can be directed in the axial direction in a low-gradienter angle in relation to the rotation axis than the common conical form. In the presented case the subzones Z1, Z2, Z3 are located stepwise in relation to each other in such a manner that between two sequential subzones there is passage in the radial direction, via which the pulp being handled transfers to the next subzone.

Fig. 4 also shows how carbon dioxide can be supplied directly to the casing that is before the blades in the flow direction of pulp (processing zone Z). The supply of carbon dioxide shown in Figs. 1 to 3 is implemented advantageously in this manner, i.e. the supply taking place before the discharge is in this case supply to the chamber before the zone Z.

In the processing zone Z the ridges of the same blade surface are substantially parallel and the ridges of the opposite blades are advantageously slightly crosswise, i.e. in a small angle towards each other in relation to the axial direction (direction of the rotation axis). When there are several subzones in the processing zone, this is the situation in the case of advantageously all subzones.

There can be more subzones than the three presented in Fig. 4. It is possible to use defibrators where the conical rotor and stator form four or five processing zones located stepwise.

A suitable raw material for the method is especially chemical pulp. After refining this pulp, which can be, for example, softwood and/or hardwood pulp, such as pine and/or birch pulp, only a part of the pulp can be processed as described above, and the remaining part is processed in a normal manner. Wood-free fine paper is manufactured of the pulp processed according to Figs. 1 or 2, the fibres of which paper contain nano-sized calcium carbonate, the concentration of which is advantageously 20 to 40 wt-% of the dry weight of the paper. Also, in addition to the fillers provided by means of the method, the paper contains normal fillers, for example normal calcium carbonates (GCC and/or PCC), which are added separately to the fibre raw material of the paper. The total concentration of mineral filler in this type of paper can be 20 to 40 wt-%, a part of which is nano-sized calcium carbonate precipitated in the fibres.

The pulp provided by the defibrator or defibrators connected in series and filled with calcium carbonate can be used either as the only pulp raw material of paper, in which case it is not mixed with other fibres, or it can be mixed with other raw material fibres of paper in the mixing tank. In addition, it is possible that the fibre pulp manufactured according to the invention is used in manufacturing multilayer paper by forming at least one surface layer of paper from it while the core layer is formed of other fibre pulp.

Claims:

1. A method for precipitating calcium carbonate in a cellulose-based fibre material, where a calcium compound is first directed to the fibre material, after which carbon dioxide is directed to this fibre material and the material is mixed in order to precipitate the calcium carbonate in the fibres, **characterized** in that carbon dioxide is directed to a fibre material, which is in a 3 to 5 % consistency, after which the fibre material if supplied in this consistency area through a mixing zone (Z) and lead in the mixing zone in question to be subject to the hydraulic cutting forces in the defibrator (C; C1, C2), the blade distance of which on said zone (Z) is in the area of 0.5 to 1.5 mm.

2. The method according to claim 1, **characterized** in that the mixing zone (Z) forms a ring-like space in the defibrator (C; C2), which widens in its diameter in the supply direction of fibre material.

3. The method according to claim 1 or 2, **characterized** in that the fibre material is directed through sequential subzones (Z1, Z2, Z3), where the blade distances decrease in the supply direction.

4. The method according to any of the preceding claims, **characterized** in that after the supply of carbon dioxide the fibre material is directed on the consistency area of 3 to 5 % through the corresponding mixing zone (Z) of at least two defibrators (C1, C2) connected in series.

5. The method according to claim 4, **characterized** in that when the fibre material has been directed through the mixing zone (Z) of the first defibrator (C1) of the defibrators connected in series, carbon dioxide is supplied to the fibre material, after which the fibre material is supplied through the mixing zone (Z) of a second defibrator (C2).

6. The method according to claim 4 or 5, **characterized** in that after the second defibrator (C2) of the defibrators connected in series, the fibre material is directed through the mixing zone (Z) of yet a third defibrator (C3).

7. The method according to any of the previous claims, **characterized** in that the calcium compound is supplied to the fibre material, the consistency of which is 3 to 5 %, or the calcium compound is added to the fibre material, the consistency of which is over 10 %, after which the fibre material is diluted to the consistency of 3 to 5 % before the carbon dioxide is directed to it.

8. The method according to any of the preceding claims, **characterized** in that the calcium compound is calcium oxide and/or calcium hydroxide.

9. The method according to claim 8, **characterized** in that the calcium compound is calcium hydroxide, which is formed by continuously forming a slurry of fine calcium oxide in water in such a manner that fresh calcium hydroxide can be continuously supplied to the process to the fibre pulp.

10. The method according to any of the preceding claims, **characterized** in that the fibre material is chemical pulp, such as softwood pulp and/or hardwood pulp.

11. A device for precipitating calcium carbonate in a cellulose-based fibre material, which comprises a fibre material processing line, where the fibre material is arranged to travel through sequential processing phases, in which case in the processing line there is first the supply (A) of calcium compound and after that the supply of carbon dioxide, **characterized** in that the supply of carbon dioxide is in the processing line at a point (B), where the fibre material is in a consistency of 3 to 5 %, in which case after the supply point the line comprises a defibrator (C; C1, C2) arranged to function on the same consistency area, which defibrator comprises a mixing zone (Z) whose blade distance is on the range of 0.5 to 1.5 mm and which is arranged to bring the fibre material under the hydraulic cutting forces by means of the movement of the blades in relation to each other.

12. The device according to claim 11, **characterized** in that the mixing zone (Z) forms a ring-like space in the defibrator (C; C1, C2), which widens in its diameter in the supply direction of fibre material.

13. The device according to claim 11 or 12, **characterized** in that the mixing zone (Z) consists of subzones (Z1, Z2, Z3) sequential in the supply direction of fibre material, where the blade distances decrease in the supply direction.

14. The device of any of the preceding claims 11 to 13, **characterized** in that after the supply point (B) of carbon dioxide in the line there are at least two defibrators (C1, C2) connected in series and provided with said mixing zone (Z).

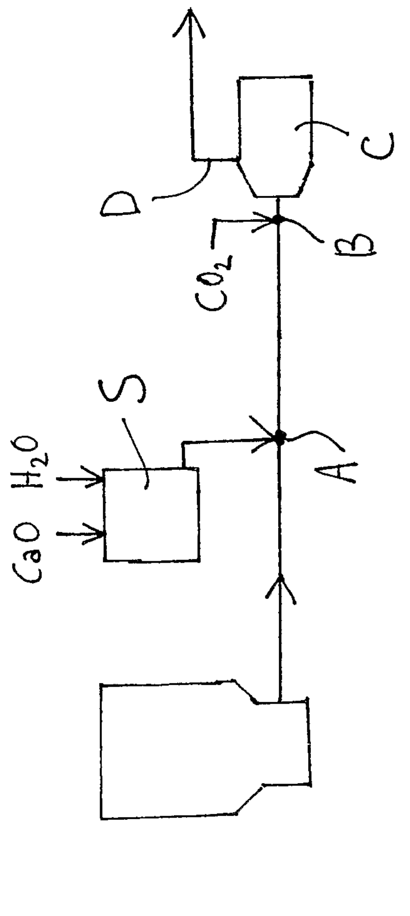

Fig. 1

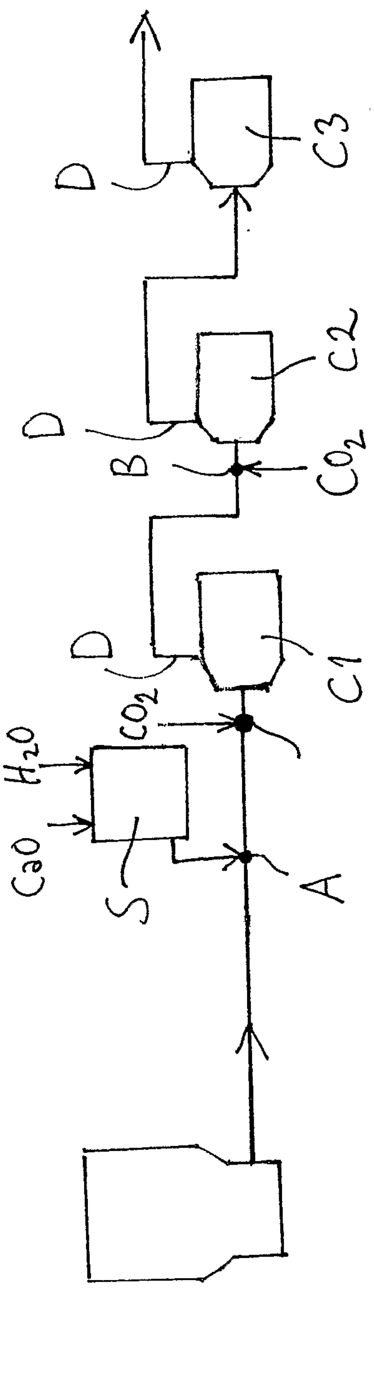

Fig. 2

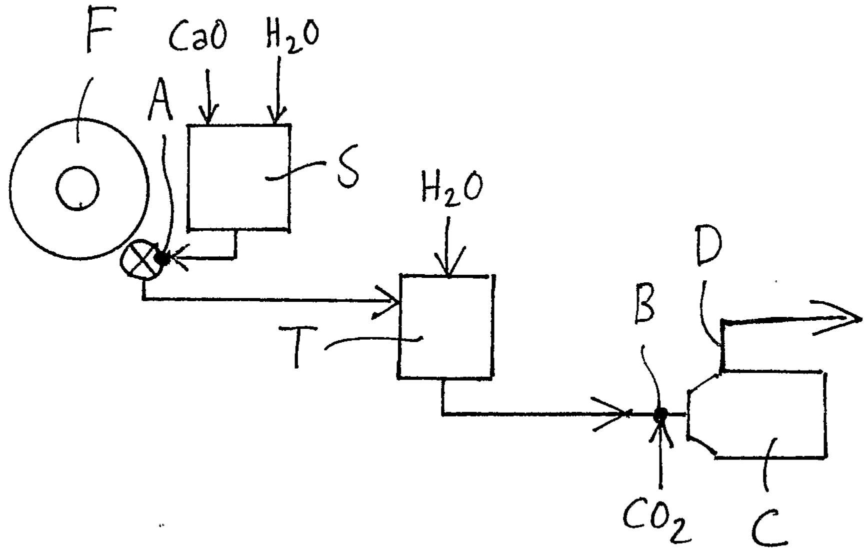

Fig. 3

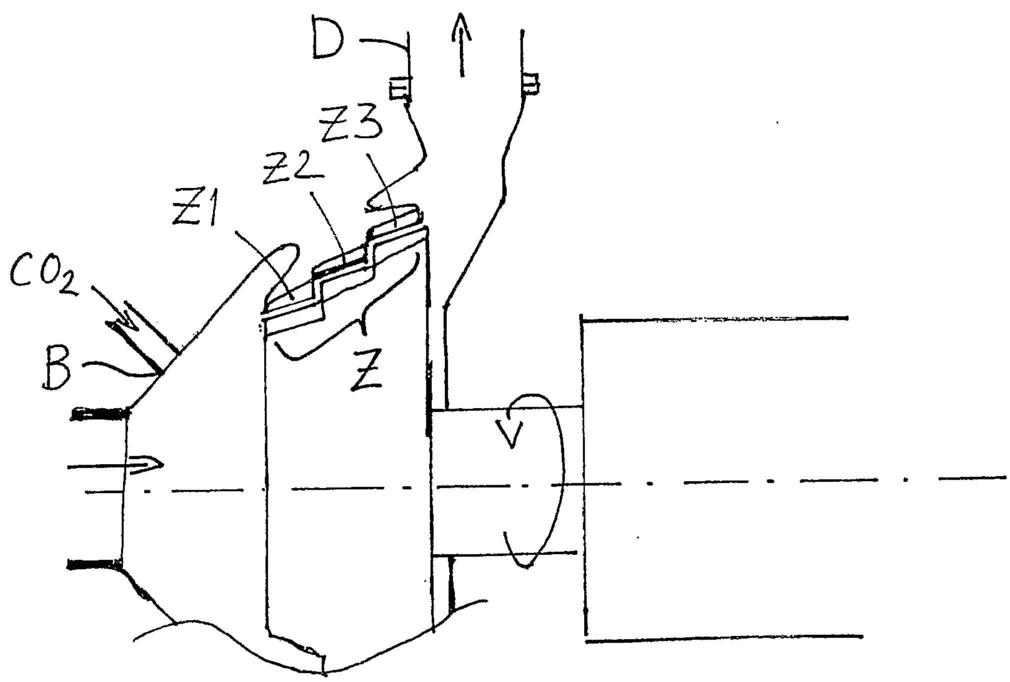

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 2004/000445

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 17/70

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03006740 A1 (VOITH PAPER PATENT GMBH), 23 January 2003 (23.01.2003), page 2, line 19 - page 3, line 9; page 6, line 13 - line 16; page 9, line 1 - line 9	1,7-11
A		2-6,12-14
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A	US 20030094252 A1 (MEENAKSHI V. SUNDAR ET AL), 22 May 2003 (22.05.2003), abstract	1-14
	--	
A	US 20020092636 A1 (JORG RHEIMS ET AL), 18 July 2002 (18.07.2002), abstract	1-14
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 November 2004	24 -11- 2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

30/10/2004

International application No.

PCT/FI 2004/000445

WO	03006740	A1	23/01/2003	EP	1409789	A	21/04/2004
				US	6413365	B	02/07/2002
US	20030094252	A1	22/05/2003	CA	2463978	A	24/04/2003
				EP	1448850	A	25/08/2004
				WO	03033815	A	24/04/2003
US	20020092636	A1	18/07/2002	US	6755941	B	29/06/2004
				AT	275660	T	15/09/2004
				DE	10033978	A	24/01/2002
				DE	50103511	D	00/00/0000
				EP	1172477	A,B	16/01/2002
				US	6599390	B	29/07/2003
				US	20020007925	A	24/01/2002
				US	20030121624	A	03/07/2003