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(54) **Process for fiber loading**

(57) The present invention relates to a process for fiber loading by creating calcium carbonate *in situ* from calcium hydroxide and carbon dioxide. The process comprises adding calcium hydroxide or calcium oxide and carbon dioxide into a suspension. In the process an alkaline alkali metal compound is added to the pulp suspension in a sub stoichiometric catalytic amount relative

to the calcium compound for promoting calcium carbonate precipitation in said pulp suspension. After calcium carbonate precipitation, the resultant fiber loaded suspension is dewatered to provide a fibrous web comprising calcium carbonate filler and an aqueous phase depleted of calcium ions.

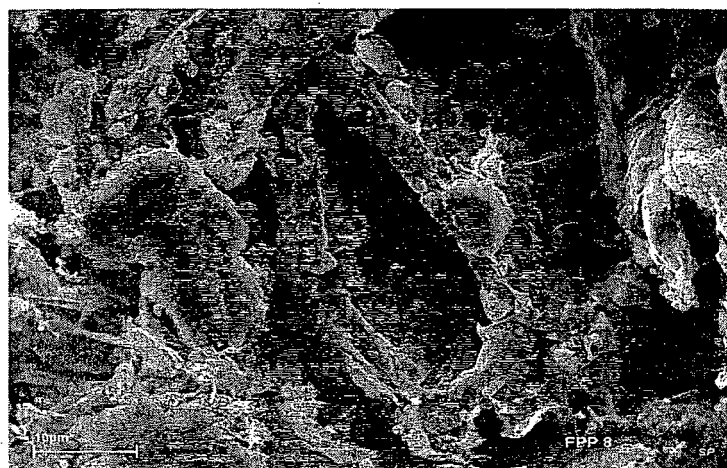


Fig. 4

Description

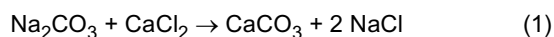
FIELD OF THE INVENTION

[0001] The present invention relates to a process for fiber loading by creating calcium carbonate *in situ* from calcium hydroxide and carbon dioxide. The process provides a filler in a pulp suspension by precipitating calcium carbonate in and on the fibers of the pulp suspension. Calcium carbonate is a much used filler in the production of paper, board and pulp. The filler improves the physical and optical properties of the finished product and the printing properties of paper. By replacing part of the fibers with less expensive inorganic material, the filler improves the economy of the papermaking.

BACKGROUND OF THE INVENTION

[0002] There are two different approaches which are used in the art for providing filler within the fibers (or fibres) of a pulp suspension. These are generally called "lumen loading" and "fiber loading". Lumen loading refers to the process of introducing minute particles of filler, often previously precipitated calcium carbonate (PCC), into the cavity or lumen of the fiber by vigorously mixing a pulp slurry containing an excess of the filler particles. Fiber loading refers to the process of creating the calcium carbonate particles in the fiber lumen and on the fiber cell walls by a chemical precipitation reaction.

[0003] Two different reactions have been used to provide the precipitation reaction of the fiber loading process, one typically comprising the reaction between sodium carbonate and a calcium salt such as calcium chloride (1) and the other typically comprising the reaction between calcium hydroxide and carbon dioxide (2):



[0004] The present invention relates to a fiber loading process utilizing the principle of the second reaction (2) mentioned above, i.e. a reaction between calcium hydroxide and carbon dioxide to precipitate calcium carbonate on and in the fibers of a pulp suspension.

[0005] The principle of creating the calcium carbonate *in situ* in the pulp by the chemical reaction between calcium hydroxide and carbon dioxide was disclosed by Klunness in US Patent 5,223,090. Calcium hydroxide or calcium oxide (which provides calcium hydroxide in water) was mixed into a dewatered pulp suspension. Then carbon dioxide was added to the mixture in a high shear pressurized refiner. In this manner about 50% of the precipitated calcium carbonate could be retained on the fiber. The rest was removed with the white water.

[0006] The fiber loading process of Klunness has since then been the subject of extensive investigations in attempts to improve features such as the speed of the process, the amount of precipitated filler, the crystal structure of the precipitate, the location of the precipitate, etc. A vast number patent applications have been filed for such improvements, some of which are mentioned below.

[0007] US-A1=2002/0088566 and US-B1.6,471,825 describe continuous processes for fiber loading by reacting calcium oxide and/or calcium hydroxide with a pressurized reactant gas selected from carbon dioxide and ozone and mixtures thereof. EP-A2-1 243 693 describes a fiber loading process, wherein the precipitation reaction is performed in the presence of a bleaching agent. US-A1-2003/0121624 describes a fiber loading process utilizing a plurality of reactors in series or in parallel to split the loading process into several smaller processes. US-A1-2004/0154770 describes the use of liquid carbon dioxide as a reactant in the fiber loading. US-A1-2008/0210391 suggests an improvement in the fiber loading process by adding the calcium hydroxide or calcium oxide at a very early stage of the papermaking, i.e. to the dry or moist fibers prior to or during the initial pulping. WO-A1-2011/151525 describes adding calcium hydroxide and carbon dioxide into water to provide an "acidic water" having a pH below 8.3. The acidic water is used for dilution of the pulp and calcium carbonate precipitation is triggered by raising the pH simultaneously with dewatering of the pulp.

[0008] WO-A1-2008/131820 describes a fiber loading process based on the principles of equation (1) above and wherein sodium carbonate reacts with a calcium salt to provide calcium carbonate. In the described process, the typically used calcium salt, i.e. calcium chloride, has been exchanged for the more alkaline calcium hydroxide. The pH may additionally be adjusted by carbon dioxide or sodium hydroxide in order to cause the calcium carbonate to precipitate primarily on the outer side of the fibers.

[0009] As noted above, the present invention relates to the Klunness reaction according to equation (2) above and wherein the carbonate moiety of the precipitate is derived from carbon dioxide. When calcium carbonate is loaded *in situ* onto and into the fibers by precipitation in this manner, a frequent problem especially in continuous papermaking processes is the presence of precipitated and non-precipitated calcium species in the aqueous phase of the pulp suspension. As indicated in US 5,223,090, the Klunness reaction resulted in only 50% of the precipitated calcium carbonate

being retained in the fibers. The rest of the calcium carbonate as well as any unreacted calcium ended up in the white waters. With ever more closed circulations of papermaking process waters, this calcium accumulates in the circulation, which in turn causes problems in the papermaking. Among these problems there may be mentioned coagulation of sticky particles, soap and ink particles, precipitation of inorganic calcium salts as a scaling, precipitation of calcium oxalate and reprecipitation of calcium carbonate, a decrease in the swelling ability of the fibers, interference with retention aids, dispersants and other charged paper additives, etc. A further complication in the Klunness process is caused by the need to use high pressure carbon dioxide in the precipitation reaction.

[0010] A mixture of fibre and calcium carbonate produced by fiber loading has better wet strength values with a specific PCC filler amount in comparison to a mixture of fibre and calcium carbonate produced in a conventional manner. Due to the improvement of wet tensile strength it is possible to introduce into the pulp suspension substantially larger amounts of fillers than previously, which typically has the effect of lowering paper manufacturing costs. The scattering of light and opacity is also improved, because there are more light scattering surfaces attached to the fibers.

[0011] In addition, there are advantageous effects on the wet tension properties of the product being produced and it is possible to decrease the dusting of the final product by the fiber loading method.

[0012] An object of the present invention is to provide a fiber loading process based on the known Klunness reaction between calcium hydroxide and carbon dioxide and wherein a high proportion of the calcium carbonate is retained in the pulp as filler in and on the fibers.

[0013] Another object of the invention is to provide a process, wherein the amount of calcium species, including free calcium ions, in the circulating process waters is low and accumulation of calcium in the process is reduced or avoided.

[0014] A further object of the invention is to produce paper having a high level of calcium carbonate filler produced *in situ* without the need for a pressurized system.

[0015] An object of the inventions is also to produce paper having a high level of ash based on calcium carbonate loading in the fibers during the papermaking process.

[0016] An object of the invention is further to provide paper having a high brightness. This is especially valuable in case of deinked paper, DIP, wherein the precipitated calcium carbonate will cover the ink particles, increase the brightness and reduce the amount of sticky particles.

[0017] An object of the invention is to provide a fiber loading process, wherein the added calcium compound is effectively utilized by substantially complete precipitation thereof in and on the fibers.

[0018] An object is also to provide a fiber loading process with a low level of calcium in the circulating process waters.

SUMMARY OF THE INVENTION

[0019] The present invention is defined in the appended claims. The invention provides a process for fiber loading of a pulp suspension by a chemical reaction between calcium hydroxide and carbon dioxide. The reaction is promoted by the use of an alkaline alkali metal compound, which creates a catalyst in the suspension to provide a fast and substantially complete precipitation of the reaction product on the fibers. After the precipitation, the pulp suspension is dewatered and made into paper, board or pulp containing the precipitated calcium carbonate as filler

[0020] *More specifically*, the invention comprises a process for fiber loading by creating calcium carbonate *in situ* from calcium hydroxide and carbon dioxide, comprising the steps of

- a. providing an aqueous pulp suspension in a process for making paper, board or pulp;
- b. adding a calcium compound selected from the group consisting of calcium hydroxide and calcium oxide into the pulp suspension;
- c. adding carbon dioxide to the pulp suspension in an amount corresponding to the stoichiometric amount or more relative to the calcium compound;
- d. adding an alkaline alkali metal compound to the pulp suspension in a sub stoichiometric catalytic amount relative to the calcium compound for promoting calcium carbonate precipitation in said pulp suspension; and
- e. after calcium carbonate precipitation, dewatering the resultant fiber loaded suspension to provide a fibrous web comprising calcium carbonate filler and an aqueous phase depleted of calcium ions.

[0021] The use of *in situ* precipitated calcium carbonate in paper improves the optical properties and the printing properties of paper and, in addition, it typically reduces production costs per manufactured ton of paper mainly due to the decreasing percentage of the amount of more expensive fibre material.

[0022] The brightness and the wet tension properties of the paper is also improved and the dusting of the paper can be reduced by the fiber loading method of the present invention.

[0023] The alkaline alkali metal compound advantageously comprises a hydroxide optionally in combination with carbon dioxide. A preferred alkali metal compound comprises sodium hydroxide or a non-stoichiometric combination of sodium hydroxide and carbon dioxide. The alkali metal compound is used in a catalytic amount. The amount of the alkali

metal compound typically corresponds to 0.5 to 20 % of the stoichiometric reaction amount of the calcium compound. The amount is preferably 2 to 10 % and most preferably 4 to 8 % of the stoichiometric reaction amount of the calcium compound. It is evident that more than 20% alkali metal compound may be added if desired but for the purpose of the invention a much smaller amount is generally enough.

[0024] The added alkali metal compound acts as a catalyst, since it is not consumed in the precipitation reaction. The catalyst is regenerated at the precipitation of calcium carbonate and recirculates in the precipitation system. Thus, the desired level of catalyst can be maintained while keeping the consumption of chemicals at a low level, which provides a cost effective process.

[0025] In addition to providing a reaction catalyst, the alkaline alkali metal compound promotes the precipitation reaction by providing a high pH.

BRIEF DESCRIPTION OF THE DRAWING

[0026] Figs. 1 to 10 show SEM images of pulps and sheets made with varying amounts of calcium hydroxide. Figs. 1 to 8 relate to Example 1, while Figs. 9 and 10 relate to Reference Example 2.

Fig. 1 shows a DIP pulp reference i.e. 0% Ca(OH)_2

Fig. 2 shows a DIP pulp according to the invention with 4% Ca(OH)_2

Fig. 3 shows a DIP pulp according to the invention with 6% Ca(OH)_2

Fig. 4 shows a DIP pulp according to the invention with 8% Ca(OH)_2

Fig. 5 shows a DIP sheet reference with 0% Ca(OH)_2

Fig. 6 shows a DIP sheet according to the invention with 4% Ca(OH)_2

Fig. 7 shows a DIP sheet according to the invention with 6% Ca(OH)_2

Fig. 8 shows a DIP sheet according to the invention with 8% Ca(OH)_2

Fig. 9 shows a DIP pulp reference

Fig. 10 shows a DIP pulp with 8% Ca(OH)_2 , without NaOH

Fig. 11 shows the pH dependent variation in the abundance of carbon dioxide, bicarbonate and carbonate in water.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The present invention relates to a process for providing calcium carbonate filler in paper, board or pulp by creating the calcium carbonate *in situ* in the process itself. The calcium in the precipitated filler derives from calcium hydroxide. The calcium compound may be added to the pulp suspension as calcium hydroxide or in the form of calcium oxide, which in water forms calcium hydroxide. The compound may be added as a powder or dissolved in water. A more uniform mixture is usually obtained, if the compound is dissolved in water. A typical calcium hydroxide solution used in the invention comprises about 5 to 15% calcium hydroxide.

[0028] The amount of calcium compound to be added to the pulp suspension is calculated based on the desired amount of filler in the final dried product. A typical amount of calcium hydroxide to add to the pulp suspension in the present invention is between 2 and 12 % calculated on the dry weight of the pulp. In an embodiment of the invention calcium hydroxide solution is added in an amount of 4 to 8 % of the dry weight of the pulp.

[0029] The calcium compound may be added all at once, or it may be added in portions along the continuous process. Calcium hydroxide is an alkaline compound and it typically raises the pH of the pulp suspension. The pH may rise to pH 10 or more, typically to 10-12 after the addition of calcium hydroxide.

[0030] The carbonate part of the filler created in the process of the invention derives from carbon dioxide. The carbon dioxide may be added in gaseous form or predissolved in water. The carbon dioxide may also be added in liquid or solid form. However, the use of gaseous carbon dioxide is preferred. The carbon dioxide may be pure carbon dioxide, but it is more economical to use a technical grade of carbon dioxide. It is also possible to utilize the carbon dioxide in smoke gas or the like by-products of the mill, as long as the impurities in the gas do not disturb the papermaking process.

[0031] In the prior art fiber loading processes pressurized carbon dioxide has been used in order to ensure a proper reaction in and on the fibers. In the present invention the carbon dioxide need not be pressurized. In a typical embodiment the carbon dioxide is mixed into the pulp suspension at normal pressure, meaning that the pulp suspension is at ambient pressure and the pressure of the gaseous carbon dioxide is no higher than needed to make it flow into the suspension. The calcium hydroxide is reacted with the carbon dioxide at ambient pressure.

[0032] Carbon dioxide dissolves in the aqueous phase of the pulp suspension forming carbonic acid and/or bicarbonate ions according to the equation:



[0033] The amount of the above species in water varies depending on the pH in accordance with the curves shown in Fig. 11. In the pH range of the present invention (pH 6 to 13), carbon dioxide has a pH lowering effect on the suspension.

[0034] The total amount of carbon dioxide added to the pulp suspension in accordance with the invention is at least equal to the stoichiometric reaction amount of the calcium compound. In order to ensure a complete precipitation of the calcium compound, the amount of carbon dioxide typically corresponds to 100 to 150 %, preferably 100 to 125 %, most preferably 100 to 110 % of the stoichiometric reaction amount of the calcium compound.

[0035] The carbon dioxide is preferably added at multiple addition points. This way the pH for the bulk of the precipitation reaction can be maintained at a high value even though a lower pH is typically desired at the end of the papermaking.

[0036] The precipitation of the calcium carbonate in the present invention is promoted by an alkaline alkali metal compound. The alkali metal compound is advantageously selected from the group consisting of sodium or potassium hydroxide, sodium or potassium bicarbonate, a mixture of sodium or potassium hydroxide and carbon dioxide, and combinations thereof. Sodium hydroxide and a premixed non-stoichiometric combination of sodium hydroxide and carbon dioxide are preferred alkali metal compounds. The sodium or potassium hydroxide is typically added in the form of a solution at a concentration of 50% or less, most typically 5 to 6%.

[0037] It is also possible to use solid sodium or potassium bicarbonate or carbonate as the alkali metal compound. However, in practice these compounds are not preferred since the handling and dissolving of these compounds in the mill is messy and provides an extra manual operation while sodium hydroxide, for instance, is a compound which is typically much used in the mill in any case and is readily available for use in the fiber loading also.

[0038] The amount of alkaline alkali metal compound used in the process of the invention is significantly less than the amount of calcium compound and carbon dioxide, since the alkali metal compound is not consumed in the precipitation reaction. Therefore, the alkali metal compound is added only in a catalytic amount. The catalytic amount of the added alkali metal compound corresponds to 1 to 50 % of the stoichiometric reaction amount of the calcium compound. In practice a very small amount of the alkali metal compound, such as 5 to 10 % of the stoichiometric reaction amount of the calcium compound is sufficient.

[0039] In case a pre-mixed combination of sodium or potassium hydroxide and carbon dioxide is used as the alkaline alkali metal compound, the mixture is preferably produced in an apparatus described in EP-B1-1461499. The mixture can be produced as a non-stoichiometric combination with a desired alkaline pH. This makes it possible to vary the pH of the alkaline compound and to control the pH and the alkalinity of the process to a desired level. A typical pH of such a non-stoichiometric combination is between 8.5 and 9.5.

[0040] The calcium carbonate precipitation reaction comprises a modification of the well known chemical reaction between calcium hydroxide and carbon dioxide:

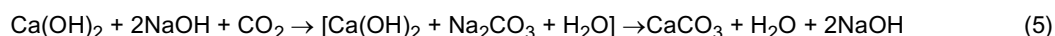


[0041] In the present invention, the above reaction is promoted by an alkaline alkali metal compound such as sodium hydroxide. The alkali metal compound is highly reactive and is believed to provide alkali metal carbonate in the aqueous phase of the pulp suspension by reacting with the carbonate ions produced by the added carbon dioxide. For sodium hydroxide the reaction can be described as:



[0042] This alkali metal carbonate is believed to act in the manner of a catalyst and to promote the formation of calcium carbonate within the lumen and in and on the cell walls of the fibers.

[0043] When the calcium carbonate precipitates, the alkali metal compound is regenerated and can act as a promoter in the next precipitation reaction. Although the chemistry of the precipitation theoretically may comprise several steps with various ionic species such as bicarbonates of alkali metal and Calcium, the promotion reaction can briefly be described for sodium hydroxide by the following equation:



[0044] Without wishing to be tied to any theory, it is believed that in the above equation, the sodium hydroxide acts to produce a transient sodium carbonate moiety, which in contacting a calcium ion of the dissolved calcium hydroxide provides an exchange of cations so that calcium carbonate is formed. Since calcium carbonate precipitates, there is a perpetual imbalance in the suspension between aqueous calcium carbonate and aqueous sodium carbonate, which drives the reaction towards calcium carbonate. This scenario is believed to create a "motor" for the formation and precipitation of calcium carbonate.

[0045] With the precipitation of calcium carbonate the alkali metal catalyst is freed and ready to act as a catalyst in the next precipitation reaction.

[0046] The alkali metal ions Na^+ and K^+ are more easily mobile in the aqueous phase and within the fibers than Ca^{2+} . The alkaline alkali metal compounds cause swelling of the fibers especially at high pH and this swelling facilitates the absorption of the larger ions Ca^{2+} and CO_3^{2-} into the lumen. The cations attach to the cell walls improving the retention of the precipitated calcium carbonate on and in the fibers. The initial precipitate is minute in size, but once some calcium carbonate has been formed on the fiber, the initial precipitate acts as a seed for further crystal growth.

[0047] At the high pH (above pH 9.5 and typically pH 10-12) prevailing at the initial precipitation, the reaction to form calcium carbonate from calcium hydroxide and carbon dioxide is quick. Some calcium carbonate is formed in less than a minute. However, the initial precipitate is very small and colloidal in consistency. In order to provide a good coverage and a substantial loading of filler, there needs to be some crystal growth. The crystals will also attach more securely to the fiber walls with time. It is the crystals on the outside of the fibers which provide the coverage providing optical benefits. However, the crystals especially on the inner side of the fiber wall provide the mass of the loading, which gives physical benefits to the fibers compared to having the same amount of filler on the outside of the fibers only. As has been ascertained by SEM images taken of pulps and sheets treated with a fiber loading process according to the invention, an exceptionally large amount of calcium carbonate crystals is found on the inside of the fiber. This is believed to reduce the negative impact that the addition of filler traditionally has on the tensile index of the fibers.

[0048] In an embodiment of the invention, the pulp suspension, after addition thereto of calcium hydroxide, carbon dioxide, and alkaline alkali metal compound and/or alkali metal catalyst, is retained as a reaction mixture in a vessel before dewatering for allowing precipitation and crystal growth of calcium carbonate. Advantageously, the retention time at least at one stage of the fiber loading process is at least 20 minutes and typically between 0.5 and 20 hours. In an embodiment of the invention, the retention time is 0.5 hours or more and preferably 1 to 8 hours, more preferably 1 to 4 hours for good fiber loading results. The crystals grow and also change crystal form with time. Thus, for best results, a retention time of at least half an hour is recommended at a pH above 9.5 and preferably pH 10 to 12. This can best be obtained by adding at least the carbon dioxide in multiple steps.

[0049] The precipitation reaction proceeds more quickly at a high pH than at a low pH. Thus, the aim is to raise the pH of the pulp suspension above pH 8 and preferably above pH 9.5 at least for the initial part of the reaction. The added calcium hydroxide has a pH raising effect, while the added carbon dioxide has a pH lowering effect. The pH may be maintained at a desired high level by adding less than the stoichiometric amount of carbon dioxide at the initial stage. Adding the alkaline alkali metal compound also counteracts the pH reduction caused by the carbon dioxide.

[0050] An ideal pH at the initial stage of the fiber loading reaction is pH 10 to 12. By using two or more addition steps for the carbon dioxide and by adding alkaline alkali metal compound, the pH of the suspension is retained at a high level until all or most of the calcium hydroxide has been consumed. When carbon dioxide is added at multiple addition points, it is preferred to make the final addition at a late point in the process such as after refining, in the machine chest or in the short circulation so that the carbon dioxide addition can be used to adjust the pH of the pulp suspension to desired lower pH level.

[0051] In an embodiment of the invention, the pH of the pulp suspension is reduced with carbon dioxide to a pH of 8.5 or less, preferably to a pH below 8 before the dewatering.

[0052] In an embodiment of the invention, at least one of the calcium compound, the carbon dioxide and the alkali metal compound is/are added in at two or more addition steps. In an embodiment, the carbon dioxide is added in two or more addition steps and the final addition of carbon dioxide adjusts the pH of the pulp suspension to a desired value between pH 6.5 and 8, preferably pH 7 to 7.5. In this embodiment of the invention it is advantageous to add the alkaline alkali metal compound of the invention in an amount to maintain the pH of the pulp suspension at pH 8 or more, preferably pH 10 or more until the final addition of carbon dioxide.

[0053] The temperature of the pulp suspension is not critical. However, calcium carbonate has a tendency to precipitate more readily at higher temperatures. Thus, good precipitation is ensured by maintaining the pulp suspension at a temperature of 40 to 60°C. Higher temperatures up to about 90 °C increases the reaction rate but this is usually too costly

[0054] The fiber loading reaction of the present invention can be performed at different positions in the papermaking process. The chemicals can be added all at the same position or at intervals along the continuous process. Calcium hydroxide may, for instance, be mixed into the pulp suspension before a refiner, for example preceding the refiner. In such a case, carbon dioxide is typically introduced after the refiner, for example following the refiner. The alkaline alkali metal compound may be added with the calcium hydroxide or with the carbon dioxide or both.

[0055] In an embodiment of the invention, the fiber loading process is performed in two separate steps. One step is early in the papermaking process and at a relatively high consistency. At least a part of the chemicals are advantageously added with the dilution water. When the addition point is early in the process, the fiber loading chemicals have a long retention time in the pulp suspension and thus time to form large crystals.

[0056] A second fiber loading step is performed later in the papermaking process at a lower consistency to precipitate more calcium carbonate onto the previously formed crystals. The second step may be performed in the short circulation or close to the short circulation for ascertaining that substantially all of the solubilized calcium is precipitated onto the fibers and that the aqueous phase of the suspension is depleted of the added calcium. This cleans up the process waters

and improves the overall process.

[0057] The chemicals of the present invention may be added to the pulp suspension in different orders. However, at least some of the alkaline compounds (the calcium compound and/or the alkaline alkali metal compound) should be added prior to the addition of carbon dioxide since carbon dioxide will dissolve much more easily into an alkaline aqueous phase. The alkaline alkali metal compound may be added prior to, simultaneously with or after the addition of calcium hydroxide. It may also be added after some carbon dioxide has already been added to the pulp suspension.

[0058] The aqueous pulp suspension which in the present invention is subjected to fiber loading may be any kind of pulp suspension, which is suitable for having calcium carbonate as filler. The present invention is also suitable for use in such processes, wherein standard fiber loading (see e.g. US 5,223,090) has typically been used. Thus, the fibers may be virgin fibers prepared by chemical, mechanical or thermomechanical pulping, etc. The fibers may also be recycled fibers such as deinked fibers (DIP), or mixtures of virgin fibers and recycled fibers.

[0059] Special benefits are provided by the present invention in connection with the use of recycled fibers, since the high level of calcium carbonate on the fibers, which is attainable with the invention, provides a good coverage on ink particles remaining on the recycled fibers and increases the brightness of the pulp. This reduces the need for cleaning of the fibers and/or the use of bleaching processes. Moreover, the calcium carbonate which adheres to the fibers will also cover sticky particles on the fibers and in the pulp suspension. When covered by the precipitate, the stickies are rendered harmless. This improves the purity of the pulp and the waters. Also the dewatering is improved. The improved process also results in improved quality of the produced paper, board or pulp.

[0060] The consistency of the pulp suspension which is subjected to the fiber loading process of the invention can vary within a broad range such as from 0.1 to 50%. High consistency pulps are typically fiber loaded in the initial stages of the papermaking. Good results have, for instance, been obtained by adding the calcium compound to a pulp having a consistency of 30 to 40%. In such a case it is advantageous to add the compound in a dilution screw to obtain a proper mixing of the calcium compound into the pulp. The dilution is typically performed with circulating process water. The calcium hydroxide/calcium oxide and, optionally, the alkali metal compound may be provided in the same dilution water or as a separate stream. A dilution to about 5 to 15%, preferably 8 to 12% is typically provided in the dilution screw.

[0061] In case the pulp which is subjected to the fiber loading process of the present invention has a lower consistency, such as 4 to 10%, a dilution screw need not be used. However, it is still important to mix the calcium compound and the alkali metal compound, if added at this stage, well into the pulp to ensure a loading of calcium carbonate all through the pulp suspension. The precipitation reaction may be performed at this consistency, or the pulp may be further diluted before addition of the compounds of the reaction.

[0062] Very good results of the fiber loading have been obtained by retaining the pulp suspension in a vessel such as a storage tank for a retention time between 0.5 and 20 hours at a consistency of 2 to 10 %, preferably 4 to 8 % after addition thereto of calcium compound and carbon dioxide as well as alkali metal compound. It was also found that at the high pH (pH 10-11) provided by the calcium hydroxide and the alkali metal compound, the gaseous carbon dioxide dissolved easily into the pulp suspension and there was no need for increased pressure as in many prior art processes.

[0063] The pulp to be treated may also have a lower consistency such as 0.1 to 4%, which is typical at the final process steps of the papermaking, such as in the short circulation. The calcium compound and alkali metal compound may be added directly to the pulp stream or to the dilution water. The carbon dioxide may be mixed into a separate water stream or it may be added directly into the diluted pulp suspension.

[0064] In an embodiment of the invention at least one of the calcium compound, the carbon dioxide and the alkali metal compound is/are added to the pulp suspension in two or more addition steps. The first addition(s) may be made at a higher consistency and later addition(s) at a lower consistency to build more calcium carbonate onto the previously precipitated filler.

[0065] In an embodiment of the invention, fiber loading is performed at two or more locations and the final one is performed in the short circulation of the process to build on an extra layer of calcium carbonate on top of previously precipitated filler. After the addition of calcium compound and alkali metal compound to raise the pH, carbon dioxide is added to the alkaline pulp. In the final papermaking stage, carbon dioxide is fed in an amount to bring down the pH of the pulp to a desired value of pH 6.5 to 8.

[0066] The alkali metal catalyst together with a stoichiometric excess of carbon dioxide ensures that the precipitation reaction is quick and complete. The aqueous phase of the pulp suspension is thereby depleted of calcium ions. Here depletion of calcium ions means that less than 20% and preferably less than 10% of the calcium ions added to the pulp suspension remain in the process water.

[0067] In an embodiment of the invention 90 to 100% of the calcium added with the calcium compound is consumed in the calcium carbonate precipitation reaction. In a typical operation of the process according to the invention also calcium initially present in the pulp suspension is precipitated so that the precipitation exceeds 100% of the added calcium and the system is effectively cleaned by the fiber loading process. In an embodiment of the invention, the precipitation reaction is continued until the amount of calcium precipitated in the process exceeds the amount of calcium added with the calcium compound.

[0068] Any minor amount of calcium ions that may remain in the water after completion of the fiber loading of the invention will stay solubilized because of the excess of carbonate in the circulating water. Due to the recirculation of the process waters, any remaining calcium ions will take part in the subsequent round of fiber loading reaction. Thus, accumulation of calcium ions in the circulating water is avoided. In fact, in the present process alkali metal ions are

circulated, while in the prior art processes calcium ions circulate and accumulate in the process waters. Since alkali metal salts are highly soluble, they do not cause problems in the papermaking process in the manner that calcium ions do.

[0069] In an embodiment of the invention the process for making paper, board or pulp is a continuous process and the dewatered fibrous web is processed to paper, board or pulp containing precipitated calcium carbonate as filler within and on the outside of the fibers.

[0070] The following examples illustrate some embodiments of the invention.

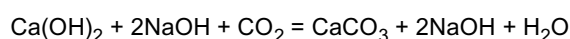
Example 1, fiber loading of DIP pulp using sodium compound catalyst

[0071] The pulps used were recycled pulp (DIP pulp) before a medium consistency (MC) refiner and reductive bleaching. For fiber loading, 300g batches of the pulp at 33% consistency were mixed with 940 g clear filtrate to 8% consistency. The samples were mixed for a few minutes with a 10% solution of calcium hydroxide added at a rate of 0 (reference), 2, 4, 6 and 8%, respectively, in the different experiments.

[0072] To the pulp samples (except reference) was added 5.4 g of a 4% solution of NaOH. This comprises a sub stoichiometric ratio compared to the amount of calcium hydroxide. For the respective experiments with 2, 4, 6 and 8 % Ca(OH)₂, the added NaOH comprised 10, 5, 3 and 1 %, respectively of the stoichiometric amount. The pulp mixtures were then reacted with carbon dioxide at normal pressure. Carbon dioxide was added until the pH had been reduced to pH 7.0-7.8.

[0073] The carbon dioxide started reacting with the NaOH and calcium hydroxide and generated insoluble calcium carbonate.

[0074] The total reaction is believed to be:



[0075] The consumption of NaOH was very low due to its role as an intermediary compound in the calcium carbonate generation. The NaOH accelerated the calcium carbonate precipitation.

[0076] Each sample was stored in sealed plastic bags at 45°C for 6 hours in a heated water bath. The above reactions continued until substantially all soluble calcium had precipitated as calcium carbonate and had caused a crystallisation process in the storage plastic bags.

[0077] After 6 hours storage the pulp was dewatered on a büchner funnel and then the pulp was pressed to obtained paper handsheets. The pulp and filtrate was analysed and the results are shown in Table 2.

[0078] The clear filtrate used for dilution of the pulp had the following content: pH 7.69, alkalinity 5.6 mmol/l, hardness 21.2 °dH and 152 mg/l Ca²⁺.

Table 1. The experimental data are summarized in the following table:

Samples	Ca(OH) ₂	DIP pulp [g]	Clear filtrate	Ca(OH) ₂ [g]	NaOH [g]	pH after Ca(OH) ₂	pH after CO ₂	pH initial	pH after 6h
	%	33%	[g] to 8%	10%	4%				
REF	0	300	940	0	0	0		7.87	7.05
2.	2%	300	940	20	5.4	12.11	7.29		6.8
4.	4%	300	940	40	5.4	12.27	7.3		6.78
6.	6%	300	940	60	5.4	12.22	7.5		6.95
8.	8%	300	940	80	5.4	12.1	7.25		6.98

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[0079] The paper hand sheets were characterized by: calcium carbonate content, ash 525°C, ash 900°C, optical and mechanical properties. SEM - Scanning electron microscopy images (Figs. 1 to 8) were obtained to identify the localization of calcium carbonate crystals into the fibre structure (lumen and fibre wall pores).

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Table 3. The paper hand sheets data and pulp mechanical and optical properties are summarized in the following table:

Measured	Analysis results							Effect of fiber loading				
	UM.	Initial	Referez	DIP + 2% Ca(OH) ₂	DIP + 4% Ca(OH) ₂	DIP + 6% Ca(OH) ₂	DIP + 8% Ca(OH) ₂	DIP + 2% Ca(OH) ₂	DIP + 4% Ca(OH) ₂	DIP + 6% Ca(OH) ₂	DIP + 8% Ca(OH) ₂	
Sheet												
EWD	sec	117.9	135.5	125.4	113.4	109.6	111.1	-10.1	-221	-25.	-24.4	
CSF	ml	156	166	176	169	173	195	10	3	9	29	
Porosity Bendtsen	ml/min	123	121	127	171	185	196	6	50	64	75	
PPS	um	8.87	8.8	8.58	8.45	8.08	8.22	-0.22	-0.35	-0.72	-0.58	
	kg/m ³	597	593	617	605	602	589	24	12	9	-4	
Tensile Index	kNm/kg	39.9	39.6	37.7	36.9	28.9	25.7	-1.9	-2.7	-10.7	-13.9	
Asch Sheet 525°C	%	8.59	8.42	12.3	15.4	17.9	19.8	3.88	6.98	9.48	11.38	
Asch Sheet 900°C	%	7.01	6.81	9.16	11	12.3	13.3	2.35	4.19	5.49	6.49	
CaC03 Sheet	%	42	43	58	65	71	75	15	22	28	32	
R457 420		57.53	57.685	59.33	61	62.445	63.015	1.645	3.315	4.76	5.33	
R457 D65		60.1	60.3	61.86	63.5	64.83	65.385	1.56	3.2	4.53	5.085	
ERIC		232.92	225.69	219.91	199.55	189.31	183.31	-5.78	-26.14	-36.38	-42.38	
Pulp												
		Initial	Ref	2%	4%	6%	8%	2%	4%	6%	8%	
Brightness		59.19	58.85	61.06	62.48	63.61	65.1	2.21	3.63	4.76	6.25	
Luminance		64.37	63.52	65.77	66.77	67.73	69.12	2.25	3.25	4.21	5.6	
DWL		575	574.72	574.52	572.69	574.41	574.24	-0.2	-2.03	-0.31	-0.48	
Purity		5.45	4.94	4.82	4.32	4.08	3.89	-0.12	-0.62	-0.86	-1.05	
ERIC		294	326.9	274.46	163.13	248.6	227.31	-52.44	-163.8	-78.3	-99.59	

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[0080] The analyses were performed according to the respective standards indicated below:

Parameter	Explanation	Test method
EWD	Dewatering time (Entwässerungsdauer)	
CSF	Freeness of paper	ISO 5267-2
Porosity Bendtsen	Porosity of paper	SCAN-P 85
PPS	Roughness of paper	ISO 8791-4
Density	Density of paper	ISO 5270
Tensile index	Strength of paper	ISO 1924-3
Ash Sheet 525°C Ash sheet 900°C	Residue on ignition at 575°C /900°C	ISO 1762 and ISO 2144
R457 420	Paper brightness	ISO brightness R457
R457 D65	Paper brightness	ISO 11475
ERIC	Effective Residual Ink Concentration of paper	ISO 22754; TAPPI 567 Pm-97 at 950 nm
Brightness, Luminance, DWL, Purity	Optical measurements	ISO 2470

[0081] SEM - Scanning electron microscopy images of the DIP pulp and sheets from the experiments above are shown in Fig. 1,2,3,4,5,6,7,8 and showing localization of calcium carbonate crystals into the fibre structure (lumen and fibre wall pores).

[0082] The images show a cross section of fibres. The white particles inside the fibres and between fibres are calcium carbonate (CaCO_3). The main part of the CaCO_3 particles are between 0.3 and 2 μm . A small amount of particles are bigger, up to 5 μm (measured on the image).

[0083] The wavelength of light is around 0.5 μm . Particles with a size close to the wavelength of light are optically active, light scattering. Particles precipitated inside and between the fibres in the sample are big enough to scatter light.

Reference example 1, DIP pulp using traditional filler

[0084] Using the same DIP pulp as used in Example 1, paper hand sheets were produced in the same manner as described in Example 1 with the exception that the filler was mixed in the conventional manner into the pulp instead of being created *in situ*. The filler was a standard calcium carbonate filler, Snowcal 45 from Omya UK Ltd. The sheets were analysed as in Example 1 and the results are shown in Table 4.

Table 4. The paper hand sheets data and mechanical and optical properties with Snowcal 45.

Measured	UM.	Analysis results			Effect	
		Initial	DIP + 2% of conventional filler Snowcal 45	DIP + 4% of conventional filler Snowcal 45	DIP + 2% of conventional filler Snowcal 45	DIP + 4% of conventional filler Snowcal 45
EWD	sec.	117.9	108.4	108.4	-9.5	-9.5
CSF	ml	156	185	185	29	29
Porosity Bendtsen	ml/min	123	163	187	40	64
PPS	μm	8.87	4.55	5.4	-4.32	-3.47
Density	kg/m^3	597	588	581	-95	-16
Tensile index	kNm/kg	39.9	36.1	33.3	-3.8	-6.6

(continued)

Measured	UM.	Analysis results			Effect	
		Initial	DIP + 2% of conventional filler Snowcal 45	DIP + 4% of conventional filler Snowcal 45	DIP + 2% of conventional filler Snowcal 45	DIP + 4% of conventional filler Snowcal 45
Ash Sheet 525°C	%	8.59	7.97	12.3	1.81	3.71
Ash Sheet 900°C	%	7.01	10.4	9.04	0.96	2.03
CaCO ₃ Sheet	%	42	53	60	11	18
R457 420		57.53	58.51	58.99	0.98	1.46
R457 D65		60.1	61.03	61.57	0.93	1.47
ERIC		232.92	214.03	206.98	-18.89	-25.94

[0085] By comparing the data of Example 1 with those of Reference Example 1, it can be seen that the papers made with fiber loading are superior to those made with a standard filler.

[0086] For 2% Ca (OH)₂, 12.3% ash in the sheet (fiber loading, Table 3), the negative impact on fiber loading on tensile index compared with conventional addition of filler (4% Snowcal 45, Table 4) on the same ash contained in the sheet, is 3.8 times lower.

[0087] Also the optical properties are superior in the fiber loading process (Table 3) compared with conventional addition of filler Snowcal 45 (Table 4).

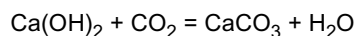
[0088] The tests show that by the fiber loading of the invention more of the added calcium filler is retained in the fibers than by a conventional method and still the fiber loaded filler has less of a negative impact on the tensile strength of the paper than the filler added by conventional means. Moreover, the optical properties of the fiber loaded papers are improved over those made with conventional filler.

Reference Example 2, DIP pulp using fiber loading without alkaline sodium compound

[0089] A DIP pulp was fiber loaded as described in Example 1 but without the use of a sodium compound as catalyst. The pulp used was a DIP pulp before the MC refiner and reductive bleaching.

[0090] For fiber loading, two 300g batches of pulp at 33% consistency were mixed with 940g clear filtrate to 8% consistency. One of the samples was mixed for a few minutes with a 10% solution of calcium hydroxide added at a rate of 8%. The other sample was mixed without calcium hydroxide (0% addition).

[0091] To the pulp sample containing calcium hydroxide, carbon dioxide at normal pressure was added until the pH was 7.15. No NaOH was added. Carbon dioxide started reacting with Ca(OH)₂ and generated CaCO₃ based on the following reaction:



[0092] Both samples were stored in sealed plastic bags at 45°C for 6 hours in a heated water bath. The reaction continued until substantially all soluble calcium had precipitated as calcium carbonate and caused crystallisation in the storage plastic bags.

[0093] After 6 hours storage the pulp was dewatered on a büchner funnel and then the pulp was pressed to obtain paper handsheets.

[0094] The clear filtrate used for dilution had the following content: pH 7.4 9, alkalinity 4.7 mmol/l, hardness 22 °dH and 157 mg/l Ca²⁺.

Table 5. The experimental data are summarized in the following table:

Sample	Ca(OH) ₂	DIP pulp [g]	Clear filtrate	Ca(OH) ₂ [g]	pH after Ca(OH) ₂	pH after CO ₂	pH initial	pH after 6h
	%	33%	[g] to 8%	10%				
REF	0	300	940	0	0		7.87	7.05
1.	8%	300	940	80	12.1	7.15		7.08

Table 6. The filtrate analysis data and pulp ash and calcium carbonate are summarized in the following table:

Analysis	Initial	6h	With chemical s	6h
	Reference		8 % Ca(OH) ₂	
°dH	19.7	23	37	25
Ca [mg/l]	140.86	164.45	264.55	178.75
Alk.	5.4			
Ash 525°C	11.0	11.21		23.8
Ash 900°C	9.21	9.22		16.3
CaCO ₃ %	37	37.5		71

[0095] The paper hand sheets were characterized by: calcium carbonate content, ash 525°C, ash 900°C, optical and mechanical properties. SEM - Scanning electron microscopy images were obtained to identify the localization of calcium carbonate crystals into the fibre structure (lumen and fibre wall pores).

Table 7. The paper hand sheets data and pulp mechanical and optical properties are summarized in the following table:

Measured	Analysis results			Effect
	UM.	Referent	DIP + 8% Ca(OH) ₂	DIP + 8% Ca(OH) ₂
Sheet				
EWD	sec.	146.4	127.0	-19.355
CSF	ml	149	152	3.5
Porosity Bendtsen	ml/min	121	134	13
PPS	(µm	8.10	7.58	-0.52
	kg/m ³	573	611	37.77
Tensile index	kNm/kg	40.5	24.5	-15.96
Ash Sheet 525°C	%	7.93	20.7	12.77
R457 420		60.11	63.42	3.31
R457 D65		62.34	65.12	2.78
Pulp				
Brightness		61.28	65.4	4.12
Luminance		66.545	71.1	4.6
DWL		574.07	572.91	-1.16
Purity		5.29	3.75	-1.54
ERIC		283.17	217.285	-65.89

[0096] For 8% Ca(OH)₂, The fiber loading without addition of NaOH provided 20.7% ash in the sheet, which gave a

negative impact on the tensile index of -15.96 kNm/kg compared to the reference (Table 7). At the same Ca(OH)_2 level, the fiber loading with NaOH provided 19.8 % ash which gave a negative impact on the tensile index of only -13.9 kNm/kg compared to the reference (Table 3). Thus, the fiber loading of the present invention reduced the tensile index significantly less (by 2,06 kNm/kg lower) than a fiber loading without addition of NaOH.

[0097] The optical properties of the paper produced by fiber loading according to the invention (Table 3) are clearly better than those provided by the fiber loading without NaOH (Table 7).

[0098] The SEM images taken of the pulps produced in Reference Example 2 (Figs 9 and 10) clearly show that less calcium carbonate has crystallized on the inner walls of the fibers when no NaOH catalyst was present.

[0099] Thus, the fiber loading of the present invention provides more calcium carbonate inside the fibers and therefore has a lesser impact on the tensile index of the paper.

Example 2, fiber loading of TGW pulp using sodium compound as catalyst

[0100] The pulps used were a TGW (Thermo Ground Wood) pulp after peroxide bleaching before the high-consistency refiner. For fiber loading, 400g batches of pulp at 33% consistency were mixed with clear filtrate to 8% consistency. The samples were mixed for a few minutes with a 10% solution of calcium hydroxide added at a rate of 0 (reference), 2, 4, 6 and 8%, respectively, in the different experiments.

[0101] To the pulp samples (except the 0% reference) was added a 4% solution of NaOH in a sub stoichiometric ratio of 5 % of the stoichiometric reaction amount of calcium hydroxide. The pulp mixtures were then reacted with carbon dioxide at normal pressure. The pH was 7.0-7.8.

[0102] The samples were stored in sealed plastic bags at 65°C for 6 hours in a heated water bath.

[0103] The reaction between NaOH, CO_2 and Ca(OH)_2 continued until substantially all soluble calcium had precipitated as calcium carbonate. Crystal growth took place inside and outside the fibers in the storage plastic bags.

[0104] After 6 hours storage the pulp was dewatered on a büchner funnel and then the pulp was pressed to obtained paper hand sheets.

[0105] The produced papers had good ash and tensile index parameters corresponding to those of the paper produced in Example 1.

Example 3, fiber loading pulp in continuous process

[0106] In a continuous papermaking process producing paper from a 50/50 mixture of DIP and virgin fibers, calcium hydroxide is mixed into the clear filtrate used to dilute the pulp suspension before the refiner which is used in the papermaking. The amount of added calcium hydroxide is 6% calculated on the dry weight of the pulp.

[0107] After refining, the pulp suspension is directed into a tank and a non-stoichiometric mixture of sodium hydroxide and carbon dioxide having its pH adjusted to pH 9 is added in an amount of 8% of the stoichiometric amount of the calcium hydroxide. Thereafter, gaseous carbon dioxide is introduced into the mixture at ambient pressure until the pH has been reduced to 8.5.

[0108] The average retention time for the pulp in the non-pressurized tank is 0.5 hours during which time most of the dissolved calcium precipitates as calcium carbonate within and on the outside of the fibers.

[0109] As the pulp passes on to the machine chest, the pulp is further diluted with water and carbon dioxide is added into the dilution water so that the pH of the pulp suspension is reduced to 7.2 due to the added carbon dioxide. Solubilized calcium hydroxide remaining in the pulp suspension is precipitated as calcium carbonate and the aqueous phase of the suspension is depleted of calcium ions. The precipitation takes place preferentially onto previously formed calcium carbonate crystals thus increasing the crystal size.

[0110] Due to the abundance of carbonate anions in the pulp suspension, the precipitated calcium carbonate stays in solid form and is retained as fiber loaded filler in the web which is subsequently produced in the wire section. The back water has a calcium ion content which is lower than that of the aqueous phase of the pulp subjected to the fiber loading process.

Example 4, fiber loading after refining and in the short circulation

[0111] In a continuous papermaking process producing paper from a mixture of DIP and virgin fibers, a 10 % solution of calcium hydroxide is mixed into the pulp suspension after refining. The amount of calcium hydroxide is 5% calculated on the dry weight of the pulp.

[0112] Simultaneously with the calcium hydroxide addition, a 5 % solution of sodium hydroxide is added to the pulp so that the amount of sodium hydroxide comprises 3 % of the stoichiometric amount of the calcium hydroxide. Gaseous carbon dioxide is added to the pulp at ambient pressure in an amount of 75 % of the stoichiometric amount of the calcium hydroxide. The pulp is vigorously mixed to provide contact of the reagents within the pulp suspension.

[0113] Due to the presence of sodium hydroxide and the low amount of carbon dioxide relative to the calcium hydroxide, the pH of the pulp suspension remains at a high level (above pH 9). The high pH and the action of the sodium hydroxide catalyst ensure that the calcium carbonate precipitation reaction is very fast.

[0114] Just before the pulp suspension enters the short circulation, additional sodium hydroxide is added in an amount of a further 2 % of the stoichiometric amount of calcium hydroxide. Then carbon dioxide is added in the short circulation in an amount which comprises the remaining 25% of the stoichiometric amount of calcium hydroxide and an additional amount to bring down the pH of the pulp suspension to pH 7.3.

[0115] Because of the presence of catalysing sodium hydroxide and because of the relatively high pH at the initial stage of the reaction, the precipitation is fast and substantially complete. The excess of carbon dioxide effectively precipitates the solubilized calcium and retains the calcium carbonate in solid form. The system is thereby cleaned from solubilized calcium ions and the fibrous web leaving the wire section is loaded with filler produced *in situ* both in and on the fibers.

Claims

1. A process for fiber loading by creating calcium carbonate *in situ* from calcium hydroxide and carbon dioxide, comprising the steps of
 - a. providing an aqueous pulp suspension in a process for making paper, board or pulp;
 - b. adding a calcium compound selected from the group consisting of calcium hydroxide and calcium oxide into the pulp suspension;
 - c. adding carbon dioxide to the pulp suspension in an amount corresponding to the stoichiometric amount or more relative to the calcium compound;
 - d. adding an alkaline alkali metal compound to the pulp suspension in a sub stoichiometric catalytic amount relative to the calcium compound for promoting calcium carbonate precipitation in said pulp suspension; and
 - e. after calcium carbonate precipitation, dewatering the resultant fiber loaded suspension to provide a fibrous web comprising calcium carbonate filler and an aqueous phase depleted of calcium ions.
2. The process according to claim 1, wherein the alkaline alkali metal compound comprises a hydroxide optionally in combination with carbon dioxide.
3. The process according to claim 2, wherein the alkali metal compound comprises a non-stoichiometric combination of sodium hydroxide and carbon dioxide.
4. The process according to claim 1, wherein the amount of the alkali metal compound corresponds to 1 to 50 %, preferably 3 to 20 %, most preferably 4 to 10 % of the stoichiometric reaction amount of the calcium compound.
5. The process according to claim 1, wherein the pulp suspension, after addition thereto of calcium hydroxide, carbon dioxide and alkaline alkali metal compound is retained as a reaction mixture in a vessel before dewatering for allowing precipitation and crystal growth of calcium carbonate.
6. The process according to claim 5, wherein the retention time is 0.5 hours or more, preferably 1 to 8 hours, more preferably 1 to 4 hours.
7. The process according to claim 5 or 6, wherein the pH of the pulp suspension is reduced with carbon dioxide to a pH of 8.5 or less, preferably to a pH below 8, before the dewatering.
8. The process according to claim 1, wherein the amount of carbon dioxide corresponds to 100 to 150 %, preferably 100 to 125 %, most preferably 100 to 110 % of the amount of the calcium compound.
9. The process according to claim 1, wherein calcium hydroxide is reacted with carbon dioxide at ambient pressure.
10. The process according to claim 1, wherein at least one of the calcium compound, the carbon dioxide and the alkali metal compound is/are added to the pulp suspension in two or more addition steps.

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11. The process according to claim 10, wherein the carbon dioxide is added in two or more addition steps and the final addition of carbon dioxide adjusts the pH of the pulp suspension to a desired value between pH 6.5 and 8, preferably pH 7 to 7.5.

12. The process according to claim 11, wherein the alkali metal compound is added in an amount to maintain the pH of the pulp suspension at pH 8 or more, preferably pH 10 or more until the final addition of carbon dioxide.

13. The process according to claim 1, wherein 90 to 100% of the calcium added with the calcium compound is consumed in the calcium carbonate precipitation reaction.

14. The process according to claim 13, wherein the precipitation reaction is continued until the amount of calcium precipitated in the process exceeds the amount of calcium added with the calcium compound.

15. The process according to claim 1, wherein the pulp suspension is retained in a vessel at a consistency of 2 to 10 %, preferably 4 to 8 % after addition thereto of calcium compound and carbon dioxide as well as alkali metal compound, and the retention time is between 0.5 and 20 hours .

16. The process of any one of the preceding claims, wherein the process for making paper, board or pulp is a continuous process and the dewatered fibrous web is processed to paper, board or pulp containing precipitated calcium carbonate as filler within and on the outside of the fibers.



Fig. 1

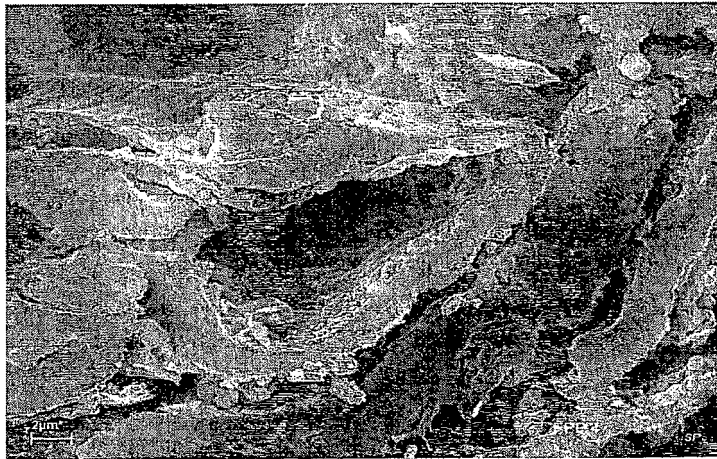


Fig. 2

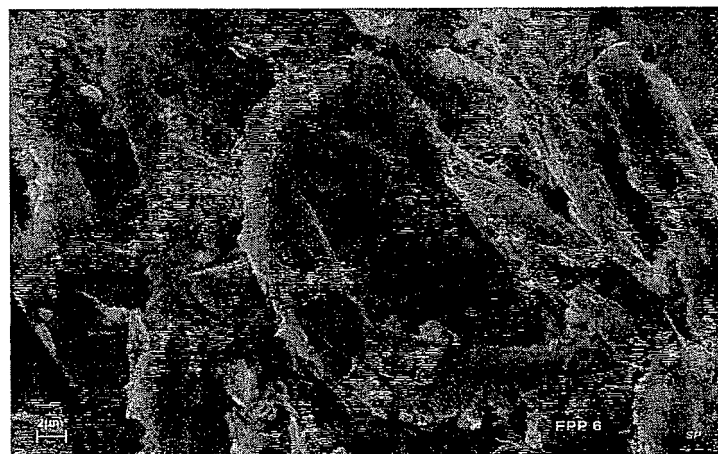


Fig. 3

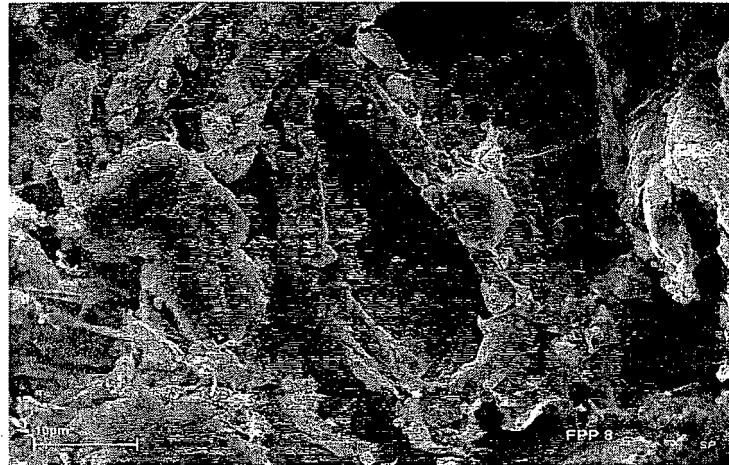


Fig. 4

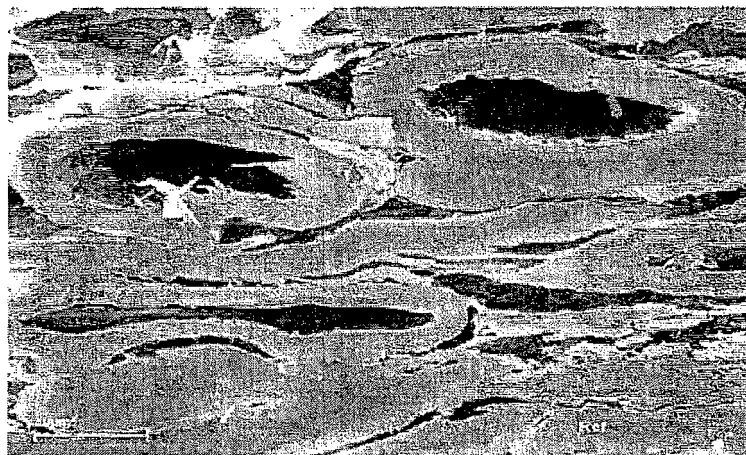


Fig. 5



Fig. 6

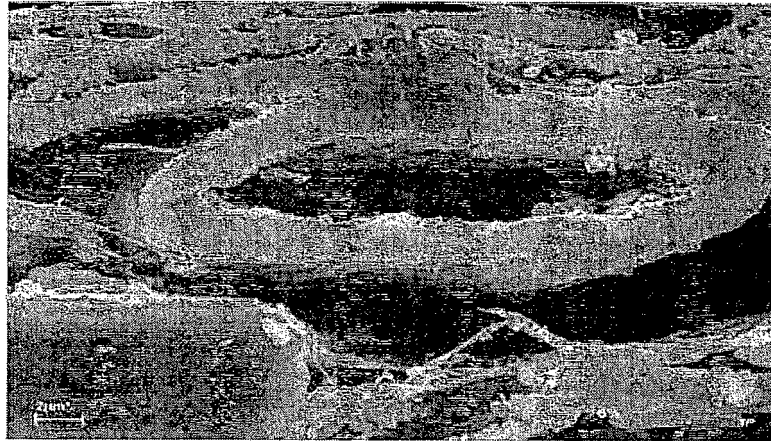


Fig. 7

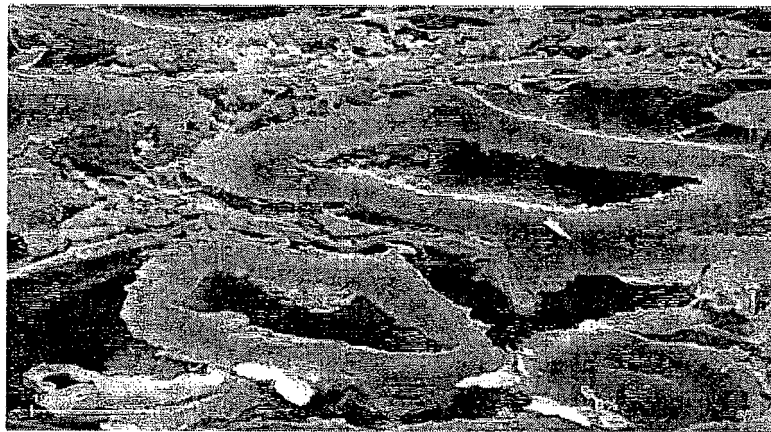


Fig. 8

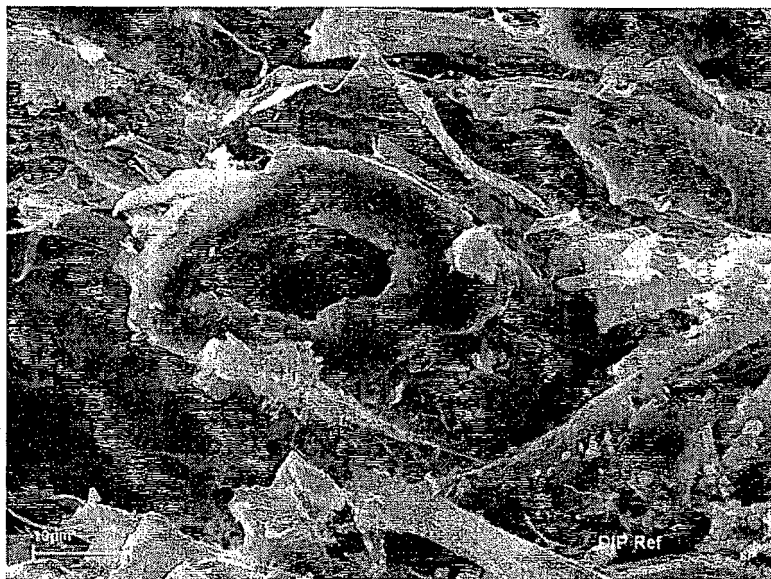


Fig. 9



Fig.10

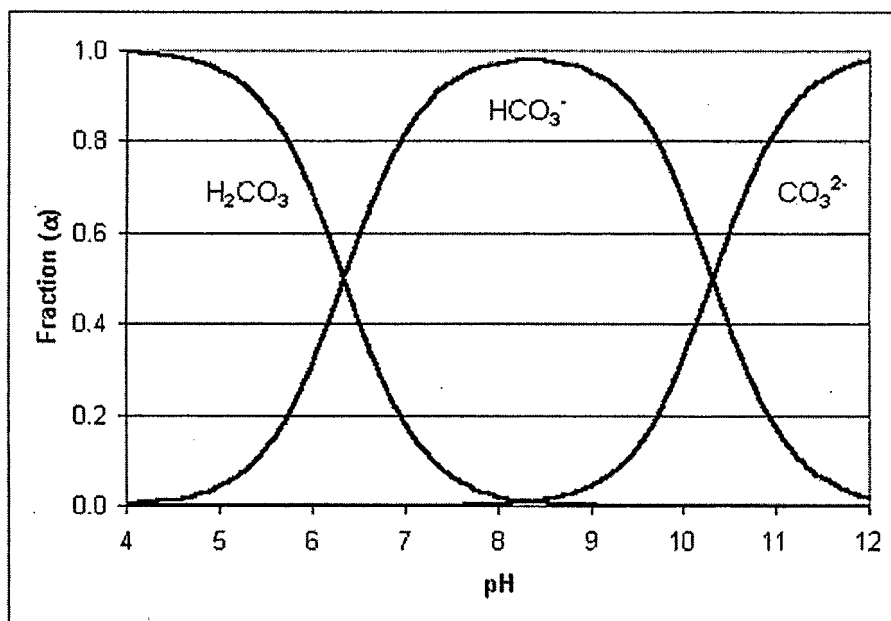


Fig.11



EUROPEAN SEARCH REPORT

 Application Number
EP 13 00 2403

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 7 October 2013	Examiner Ponsaud, Philippe
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 : non-written disclosure P : intermediate document 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 & : member of the same patent family, corresponding document			

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

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