The present invention relates to a fibre product that contains pulp fibre or wood fibre, wherein filler particles are attached between the fibres and to the fibrils, part of the particles consisting of chemically structured kaolin agglomerates or granules, and a part consisting of carbonate that is formed from a corresponding oxide or hydroxide by means of carbon dioxide. The invention also relates to a manufacturing method of such a fibre product.
PROCESS FOR MANUFACTURING PAPER AND BOARD

CROSS REFERENCE TO RELATED APPLICATIONS


FIELD OF THE INVENTION

[0002] The present invention relates to a fibre product that contains pulp or wood fibre, and to the manufacturing method of this product, wherein filler particles are attached to the pulp fibres or wood fibres as well as to fibrils, after which paper or board is produced from the fibre pulp.

BACKGROUND

[0003] Typically, the fillers or pigments that are used in the manufacture of paper and board have an average particle size of less than 5 μm and a light colour. The most typical fillers include kaolins, talcs, ground calcium carbonate, and precipitated calcium carbonate. In addition, there are more expensive, so-called special pigments, such as precipitated aluminium silicates, satin white, and titanium dioxide. Drawing an exact line between fillers and coating pigments is difficult, however, roughly speaking, fillers have a larger size than the pigments that are used in coating. From the point of view of a maximum light scattering, an optimal particle size for the most common fillers and coating pigments would be 0.4-0.5 μm. Typically, the average particle size of the coating pigments is 0.5-1 μm and that of the fillers 1.5-4 μm.

[0004] One problem with the fillers commonly used in the manufacture of paper and board products is that they weaken the final product. In particular, paper grades that have large filler contents, such as copying papers and specific magazine papers, would generally need improved stiffness compared to the present situation. The efforts to achieve lighter basis weights in the manufacturing of paper and cardboard also emphasize the need for stiffness. Generally, the stiffness of paper weakens as the amount of filler in the paper increases or if the basis weight is reduced. This decrease in stiffness together with the decrease in strength constitutes the major problems with quality in the use of fillers in printing papers. Conventionally, this problem has either been solved by adding a separate strengthening additive or decreasing the amount of filler. On account of the price and properties of pulp, this is not profitable, however.

[0005] The most common clay mineral that is used as filler in the manufacture of paper and board is kaolin that mainly consists of kaolinite. The kaolin mineral has a two-layer, laminar structure that comprises a tetrahedral layer of silicon dioxide and an octahedral layer of aluminium oxide. The layers are interconnected by oxygen atoms. Because of the silanol groups of the surface of kaolin, the surfaces of the kaolin mineral are negatively charged and its edges are positively charged, when suspended in water. Kaolin can be manufactured by dry or wet processes; however, in the wet process, it is possible to have a greater chemical effect on the final brightness of kaolin at the various process stages. The most common commercial kaolin grades include water-washed, delaminated, calcined, and chemically structured kaolins. The water-washed grade often contains several kaolin sheets that are attached to each other at their surfaces. In the delaminated grades, kaolin surfaces are separated by grinding them into smaller groups and single kaolin sheets. The calcined kaolins are made by allowing kaolin sheets, which have a conveniently small particle size distribution, to partly melt to each other at a temperature of about 1000°C. At a temperature of over 450°C, the structure of kaolin crystals begins to change. Kaolin crystals that are heated at a temperature of about 500-800°C are called metakaolin. The advantages of metakaolin and calcined kaolin are particularly visible as an improvement in brightness and opacity compared with water-washed and delaminated kaolins. This is based on the fact that, between the kaolin sheets in the calcined kaolin, there are interfaces of air and kaolin which are effective in scattering light. The pores formed in the structure of the structured kaolins further help in the setting of ink. The manufacture of chemically structured kaolins is based on the formation of the same interfaces, but in this case, the interfaces can be chemically bound to each other—not by means of high temperatures. The light scattering efficiency of the chemically structured kaolins is normally between that of the delaminated and calcined kaolins.

[0006] The greatest disadvantage of using kaolin, as well as other fillers, is the weakening of the strength of the paper or board structure when replacing the mass with filler, in particular. This is because fillers prevent the formation of hydrogen bonds between the fibres by attaching themselves to the surfaces of the fibres.

[0007] In the specification FI 20020566, it has been proven that by using structured filler agglomerates of an average particle size of over 5 micrometres, improved strength of the fibre network is achieved with the same filler content than with normal fillers of less than 5 micrometres. The specification FI 20085227 further shows that, by improving the ability of the surfaces of the filler agglomerates of over 5 micrometres to form hydrogen bonds, further improvement in the strength and stiffness of the fibre network is achieved.

[0008] In this way, filler particles are obtained, which have a suitable size category to fill the openings between the pulp fibres. The required strength is thus achieved for the fibre product, and at the same time, part of the pulp can be replaced. Generally, in prior art, achieving the strength has been sufficient. Another purpose of fillers and additives, however, is the retention which is very difficult to improve in connection with improving the strength of the product.

[0009] In the manufacture of paper or board, it is known to form the paper or board product by dewatering solid matter pulp. Of all the raw materials, the amount of water is clearly the greatest and the idea is to remove it as quickly as possible from the end product by means of the wire, press and dryer sections. Dewatering is one of the most important factors that influence the economy of papermaking, and the idea is to influence it in a chemical manner through various flocculants and coagulants, among others. Concerning mechanical dewatering, the purpose is to influence it by means of the wire, press, and dryer sections. The more effective dewatering also leads to a reduction in the need for drying energy in the dryer section.

[0010] The various fillers also bind less water than fibres do, contributing to the financial advantage of their use due to the accelerated dewatering. In the wire, press, and dryer sec-
tions, the lower water retention capacity is visible as a quicker dewatering and, thus, lower energy costs in drying, when the filler is used.

[0011] Generally, the fillers and fibres have an anionic charge. Therefore, to improve the filler retention, a cationic charge in the form of ions or polymers should generally be supplied to the pulp to bind the filler to the fibre network. In printing papers, the filler contents are about 30%, calculated from dry fibre. The retention can be divided into a mechanical and chemical one, of which the chemical retention definitely has more significance. The mechanical retention has more meaning for boards of a high basis weight.

[0012] The decrease in strength and stiffness of the paper or board product when replacing the fibre with filler is mainly caused by the fact that the fillers weaken the formation of hydrogen bonds between the fibres, since the surfaces of the fillers do not form hydrogen bonds. At present, the filler is added directly to the pulp. In the wire section, only part of the added filler is attached to the finished paper or board web. The rest of the filler travels through the white water system to finally constitute part of the finished paper or board structure, but then the risks of various runnability problems have increased mainly due to the attachment of various hydrophobic substances to the fillers of the white water system. In the paper or board machine, the runnability problems caused by this usually appear as contamination, breaks, of the wires and felts, for example. Part of the filler of the white water system also finally burdens the sewage treatment plant, because it is never entirely carried out of the process along with the finished paper or board.

[0013] Consequently, there is a need for a fibre product, wherein the filler would attach itself to the fibre more effectively and, at the same time, would give the product advantageous strength properties that would preferably be further improved compared to the known solutions.

SUMMARY

[0014] An object of the present invention is to provide a new paper or board product that has good strength and high opacity.

[0015] An object of the present invention, in particular, is to provide a new paper or board product that contains, as filler, granules that attach between the fibres and carbonates that attach to the fibres.

[0016] The object of the present invention is to utilize an aqueous, carbonate-bearing salt composition to suspend structured kaolin in the manufacture of the paper and board products. In this way, as quick as possible dewatering and high wire retention in the wire section and the improvement of specific quality properties of paper and board are ensured. To incorporate the kaolin sheets, among others, latexes can be used as binders, by means of which the kaolin sheets and stocks can be attached to each other to form granules or agglomerates from the kaolin slurry by means of a mixing technique or spray drying. The purpose is to provide structured kaolin with an average particle size of over 5 micrometres. The structured kaolin thus dried can then be converted into calcined kaolin or metakaolin by heating it in a furnace. In the manufacture of paper or board, an improvement is achieved by using the structured kaolin that is suspended in the aqueous solution, according to the invention, whereby quicker dewatering and higher retention are utilized in the wire section. From the kaolin slurry that is prepared in the aqueous salt composition, carbonate filler is precipitated to the fibre structure by means of an increase in the pH, pressure or temperature, preferably at the tail of the wire section and/or after the press section. The goal is to introduce a desired amount and distribution of precipitated carbonate filler into the lumen and fibrils of the fibre structure, whereby the effect of structured kaolin that weakens the stiffness can be prevented. At the same time, the carbonate filler thus created increases the brightness, opacity, and printability that are achieved by using structured kaolin alone. In an ideal paper or board structure, the carbonate filler thus created would be contained in the fibrils of the fibres, increasing the stiffness, among others, and the structured kaolin would be contained in the holes of the fibre network, whereby the weakening of the strength and stiffness of the fibre network caused by the prevention of the formation of hydrogen bonds between the fibres of the filler would be lesser than when using fillers or pigments with an average particle size of less than 5 micrometres.

[0017] The present invention thus relates to a fibre product that contains pulp fibre or wood fibre, the product preferably being paper or board, and to the manufacturing method of this product, wherein filler particles are attached between the pulp or wood fibres and to the fibrils, after which the said paper or board is produced from the pulp.

[0018] To be more precise, the fibre product that contains pulp fibre or wood fibre is such that filler particles are attached between the fibres and to the fibrils, part of them having chemically structured kaolin agglomerates or granules, and part having carbonate.

[0019] The manufacturing method of the fibre product includes adding an oxide or hydroxide to an aqueous solution to form a hydroxide slurry, and reducing the pH of the solution to a range of 6.0-8.3 by convaying carbon dioxide to the solution so that the content of the salts of carbonic acid formed from the carbon dioxide and the hydroxide slurry is at least 0.01%, calculated from the total weight of the solid matter of the solution, whereby a salt composition is formed; suspending kaolin sheets or stacks or both in water together with a binder, whereby a kaolin composition is formed; producing kaolin drops in a spray drier from the kaolin composition, which is formed from the kaolin sheets or stacks or both and contains the binder, whereby excess water also evaporates, whereby structured kaolin particles are formed, or forming these structured kaolin particles by means of a mixing technique from the kaolin sheets or stacks or both, which are in the form of the slurry in the salt composition described above or its dissolved portion, with the binder; admixing the formed structured kaolin particles together with the salt composition or its dissolved portion to a paper or board pulp, whereby a fibre dispersion is formed; and precipitating the carbonate from the salt composition into particles in the dispersion while the dispersion is filtered, pressed, and dried into paper or board.

[0020] The present invention is multifunctional and it improves various properties: the quality properties of paper and board and the economic activity of the manufacturing process. By combining carbonates of a suitable size with particles of structured kaolin of a suitable size, the invention makes it possible, among others, to improve the brightness, opacity, and printability; at the same time, the dewatering can be accelerated and the retention improved in the wire section. An additional advantage of the use of kaolin also comprises the effect of further improving the stiffness, opacity, brightness, and printability that are given to the fibre structure by the
precipitated carbonate filler. At the same time, part of the fibre of the end product is now replaced with the filler without weakening the strength properties.

DETAILED DESCRIPTION

[0021] The present invention relates to a fibre product that contains pulp fibre or wood fibre, wherein filler particles are attached between the fibres and to the fibrils, part of the particles consisting of structured agglomerates or granules of kaolin, metakaolin or calcined kaolin, and part consisting of the salts or esters of carbonic acid or a combination thereof, preferably the various states of carbonate.

[0022] This invention proves that when the aqueous salt composition is used in the manufacture of structured kaolin slurry and when the pH of the paper or board pulp that is diluted with this composition is increased with an alkali and/or the temperature is increased, possibly simultaneously with increasing the solid matter content of the pulp, a carbonate filler can be precipitated to the paper or board structure. This precipitated carbonate filler has a positive effect on the brightness, opacity, printability (the absorption properties of the ink), thickness, and stiffness of the paper or board product.

[0023] The product can contain as much as 25% by weight of structured kaolin particles from the dry matter, at least 5% by weight from the fibre. They are essentially spherical in shape and have a size of >5 μm, preferably 10-40 μm, more preferably 20-40 μm. They consist of chemically structured kaolin agglomerates or granules, which are optionally processed so that a part thereof, preferably the surface, is calcined or changed into metakaolin. The kaolin of the filler is preferably dry-calculated, water-washed, dry-classified, or treated by means of two or more of the said treating methods.

[0024] The amount of carbonate in the product is at least 0.01% by weight from the dry matter, for example 0.01-5% by weight, particularly 0.01-3% by weight. At normal pressure, the salts of carbonic acid comprise carbonate or bicarbonate salts, preferably bicarbonate and colloidal carbonate. They may have an average particle size of <0.3 nm, most suitably <0.1 nm.

[0025] “Colloidal carbonate particles” in the present application refer to carbonates that have a small average particle size of less than 300 nm, preferably less than 100 nm.

[0026] The salts or esters of carbonic acid are preferably made of a corresponding oxide or hydroxide and they consist of an inorganic or organic salt or a composite or mixture of several salts, most preferably calcium salt or magnesium salt or a mixture thereof.

[0027] According to a preferred embodiment of the invention, the filler particles are attached to each other and to the fibres by a binder, which is preferably latex, silicon dioxide, alum or aldehyde or a mixture thereof, most preferably in an amount of 0.5-50% by weight.

[0028] The product can further contain other retention agents or flocculating or coagulating microparticles or a mixture thereof; preferably at least microparticles, most preferably together with conventional retention agents.

[0029] Various synthetic and natural polymers function as retention agents in the invention. Natural polymers are generally called polysaccharides. Examples of these include starch, which is the most commonly used natural polymer in the manufacture of paper and board, if fibres are not taken into account. Regarding synthetic polymers, polyacrylamides should be mentioned. Polymer, in particular, is selected from a group of polyacrylamide, polyethyleneimine, starch, polydadmac, polyacrylamide, polyamine, starch-based coagulant, any copolymer of the above or a mixture of two or more such polymers or copolymers. The polymer is most preferably polydadmac, polyacrylamide, polyamine or the copolymer of two or more of these.

[0030] Inorganic, so-called microparticles are preferably used together with these polymeric retention agents to improve the dewatering, retention, and formation. Of these inorganic microparticles, colloidal silicon dioxide (polysilicic acid, silicon dioxide sol, microgel, etc.) and bentonite are especially well-suited to this purpose. Other alternatives include other sols, gels, microgels, silicic acids, and polysilicic acids or mixtures thereof that contain bentonites or silicon dioxides.

[0031] The product can also contain one or more chemicals known as such, which are selected from a group of aluminium compounds, stock sizes, surface sizes, antisilfume agents, colouring agents, starches, optical brighteners, dispersing agents, anti-float agents, plastic pigments, and conventional fillers and coating materials.

[0032] The present invention also relates to the manufacturing method of such a fibre product, wherein oxide or hydroxide is added to the aqueous solution to form hydroxide slurry, and the pH of the solution is decreased to a range of 6.0-8.3 by conveying carbon dioxide to the solution, so that the content of the salts of carbonic acid formed from the carbon dioxide and hydroxide slurry is at least 0.01%, calculated from the entire weight of the solid matter of the solution, whereby a salt composition is formed;

[0033] kaolin sheets or stacks or both are suspended in water together with a binder, whereby a kaolin composition is formed;

[0034] kaolin drops are produced in a spray drier from the kaolin composition, which is formed from the kaolin sheets or stacks or both and which contains the binder, whereby excess water is also evaporated, whereby structured kaolin particles are formed; or these structured kaolin particles are formed, by means of a mixing technique, from the kaolin sheets or stacks or both that are in the form of slurry with the binder in the above-described salt composition or its dissolved portion;

[0035] optionally, the spray-dried structured kaolin particles are mixed with the salt composition described above or its dissolved portion;

[0036] the structured kaolin particles thus formed are admixed, together with the salt composition or its dissolved portion, to the paper or board pulp, whereby a fibre dispersion is formed; and

[0037] the carbonate from the salt composition is precipitated into particles in the dispersion, while the dispersion is filtered, pressed, and dried into paper or board.

[0038] Briefly, in the method according to the present invention, the solid matter of the paper or board pulp is diluted with the kaolin composition that is suspended in the salt composition, according to the invention. The salt composition consists of the states of carbonate, i.e., carbonates and bicarbonates, and calcium or magnesium ions or a mixture thereof, which are added to and produced in the aqueous solution at a pH that remains below 8.3 throughout the production state. These states of carbonate include, among others, colloidal-size carbonate particles, bicarbonate ions, carbonate ions and carbonic acid, which are formed in the aqueous solution, when the pH is below 8.3.
In the invention, slurry of structured kaolin is added to a salt composition similar to the one described above, at the manufacturing stage of the paper or board product that is before the headbox of the paper machine, or the structured particles are formed in this salt composition.

The slurry of structured kaolin is very useful, for example, in accelerating the dewatering and improving the retention in the wire section of the paper machine. For example, in the drying of paper or board, carbonate can be precipitated to the fibre structure from the salt composition, the carbonate enhancing the light scattering efficiency of kaolin, whereby the opacity and brightness increase, while the total amount of filler remains the same. In addition to the increase in temperature occurring in the drying of paper and board, carbonate can be precipitated either by increasing the pH (e.g. by using an alkali) or by increasing the pressure in the wire, press, and dryer sections. It is essential, however, to try to keep the pH of the paper or board manufacture on the acid side in the long and short cycles. Kaolin slurries in aqueous solutions are naturally acidic, whereas calcium carbonate and talc slurries are alkaline. In case the pH of the circulation water is to be increased by increasing the temperature or pressure, or by increasing the pH by adding alkali, this is not carried out before the headbox or the wire section of the paper or board machine.

Said "aqueous solution" can be any watery solution.

According to a preferred embodiment of the invention, however, this aqueous solution is raw water, chemically or mechanically purified water, water filtered water that is purified to various degrees of purity, or another kind of water used in the paper factory, or a mixture thereof, preferably filtered water or process water, from which the solid matter is separated or has been separated.

According to another preferred embodiment of the invention, the said aqueous solution employed consists of chemical pulp (sulphite or sulphite pulp), mechanical or semi-mechanical pulp, pulp manufactured by means of alkalis, recycled fibre, deinked pulp (purified by washing or flotation), nano-cellulose, coated reject, uncoated reject or a mixture thereof.

Particularly according to this second preferred embodiment, paper pulp is first manufactured from the aqueous solution, the solid matter of the paper pulp being mixed with the light paper pulp, whereafter the stages of the method mentioned above are carried out.

In addition to the said aqueous solution, the "salt composition" thus contains salts of carbonic acid. The salt composition preferably consists of the carbonates or bicarbonates of magnesium or calcium or a mixture thereof, and it is preferably manufactured by adding the slurry of oxide or hydroxide to the aqueous solution and by conveying carbon dioxide to the solution, so that the pH in the aqueous solution remains essentially below 8.3 throughout this stage, whereby bicarbonate and colloidal carbonate are formed, their average particle size being <0.3 nm, most preferably <0.1 nm.

In paper and board machines, the aim is usually to keep the pH of the white water system within 6-8. For example, the chemistry of carbonate ions and the buffering of pH provided by the same are then utilized.

At an acidic pH, soluble carbon dioxide (CO₂) and, to a minor extent, carbonic acid (H₂CO₃), are the main states of carbonate. In the neutral (on both sides of a pH of 7) and alkaline ranges, bicarbonate or hydrocarbontate (HCO₃⁻) is the main state of carbonate all the way to a pH of 10. "Main" means that at least 50% by weight of the states comprise carbonate. In a very alkaline range (pH >10), carbonate (CO₃²⁻) is the main state. When moving from the alkaline range towards the acidic one, essentially all of the CO₃²⁻ has been converted into a form of HCO₃⁻ at a pH of about 8.3. In the most important pH range of the paper and board manufacture, the pH of 6-8, bicarbonate (HCO₃⁻) is thus the prevailing state.

"Structured kaolin particles" are produced from the kaolin sheets or stacks of the kaolin composition, which are possible further processed, so that at least part of the kaolin, preferably of its surface, is converted into metakaolin or calcined kaolin.

The granules or agglomerates of structured kaolin are manufactured by spray-drying the kaolin slurry by means of a binder. For the spray-drying, a rotating atomizer, discharge nozzles, a double-fluid nozzle, ultrasound or a combination of the foregoing can be used.

Metakaolin or calcined kaolin can be manufactured from these granules or agglomerates by heating, in a furnace, the spray-dried kaolin granules or agglomerates or those that are manufactured by means of the binder using the mixing technique. In the manufacture of "structured" kaolin, i.e., spray-drying, raw materials other than kaolin can also be used. Before spray-drying or using the mixing technique together with the binder, for example, calcium carbonate, titanium dioxide, talc or silicon dioxide or several substances, among others, can be added to the kaolin slurry that is manufactured in the aqueous solution, before manufacturing the granules or agglomerates.

In addition to these granules and agglomerates, the "fibre dispersion" contains a source of fibre, binder, and the salt composition mentioned above. In the present invention, the fibres can consist of chemical pulp or mechanical pulp. For example, sulphate and sulphite cellulose fibres, dissolving pulp, nano-cellulose, chemic-mechanical pulp (CTMP), thermomechanical pulp (TMP), pressure groundwood (PGW), ground pulp, recycled fibre, or fibres of deinked pulp can function as fibres. The binder has settled on the surfaces of the formed kaolin particles, and it functions by binding the particles to each other and, particularly, by binding the particles to the fibres.

Flocculants, coagulants or microparticles or a mixture or a copolymer thereof can be added, as a retention agent, to the aqueous solution or the fibre dispersion, in an amount of at least 0.01%, particularly about 0.01-3%, calculated from the total weight of the solid matter of the solution or dispersion, preferably at least microparticles, most preferably together with conventional flocculants or coagulants.

One or more chemicals known as such can also be added to the fibre dispersion, the chemicals being selected from a group of aluminium compounds, stock sizes, surface sizes, colouring agents, starches, optical brighteners, plastic pigments, natural and synthetic polymers, and fillers and coating materials.

At the drying stage of the paper or board manufacture or by increasing the pH, the bicarbonate ions contained in the salt composition or mixed with the fibre dispersion can be converted into carbonate particles. Correspondingly, when increasing the temperature, carbon dioxide is released and the bicarbonate reacts with free calcium or magnesium ions according to the following equation:

\[
Ca^{2+} + (HCO_3^-) \rightarrow CaCO_3 + CO_2 + H_2O.
\]
When the pH is increased with an alkali, e.g., NaOH or Ca(OH)$_2$, the carbonate particles can be precipitated according to the following reaction equations:

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- + 2\text{NaOH} \rightarrow \text{CaCO}_3 + 2\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}.
\]

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}.
\]

The carbonate particles thus formed fit between the fibrils and fibres, keeping the fibrils in their outward-oriented positions and giving the structure of the paper or board opacity, brightness, stiffness, and thickness (bulkiness). The carbonates on the surface of the paper or board, in particular, improve the adsorption of the printing ink. Part of the precipitated carbonate is also inside the lumens and pores of the fibres. Structured kaolin, in turn, fills the holes that remain between the fibres of the fibre network, whereby the strength and stiffness are reduced less than when using, e.g., pure fillers with an average particle size of 3 micrometres or less.

The dispersion formed from these ingredients is then mixed to form the pulp, which at the last stage of the method according to the invention is filtered, pressed, and dried into the paper or board product. At this stage, usually, openings of about 10 micrometres remain between the fibres. The kaolin agglomerates of a size of about 10 micrometres, which are utilized in the present invention, however, drift from the pulp into these openings when water is removed, thus increasing the surface area in which the hydrogen bonds can be formed. With commercial fillers, the decrease in strength is more pronounced, since there is less surface area between the fibres for the formation of hydrogen bonds. Therefore, structured kaolin with an average particle size of about 15 µm is used in the present invention.

The following examples describe the specific preferred embodiments of the present invention. They are intended to illustrate the benefits and advantages achieved by the invention, and not to limit the scope of the invention.

**EXAMPLES**

**Example 1**

Manufacture of Structured Kaolin and Acidic Water

In this example, the salt composition, which hereinafter is called acidic water (below, also “AW”), was made in ion-exchanged water. First, 25 kg of ion-exchanged water were weighed into each one of closable plastic cans (of a volume of 30 litres). 170 g of burnt lime (CaO) were added thereto, having been slaked in 600 g of ion-exchanged water at 45°C before the addition. By adding carbon dioxide to the weak calcium hydroxide slurry thus formed, Ca(OH)$_2$, the pH was dropped from about 12 to 6.3. This solution was allowed to sediment for 12 hours, after which the colloidal portion that had not sedimented was separated from the can. The precipitate that sedimented on the bottom was not used in the tests.

Dry Covergloss (Kamin L.L.C) kaolin powder was suspended in ion-exchanged water to a dry matter content of 20%. In the elutriation, 0.2% of the Dispex N40 (BASF) dispersing agent and 8% of latex (Acronal S505, BASF) were used, calculated from the weight of the kaolin. After this, the suspension was spray-dried (Niro, mobile minor). The feed rate of the suspension was 50 ml/min, the rotation speed of the atomizer was about 25000 rotations per minute, the temperature of the drying air was 250°C, and the temperature of the output air was 110°C. The dried, structured kaolin (below, “struc”) was cooled to room temperature and suspended in acidic water into slurry of 20%. The average particle size of the structured kaolin thus manufactured (struc+AW) was 15 micrometres (Sedigraph 5120, Micromeritics).

**Example 2**


In this test series, a Valley grinder was used to first grind a mixture of bleached pine pulp and bleached birch pulp to an SR number of 30. The amount of pine pulp from the weight of the pulp was 30% and that of birch pulp was 70%. The pulp was ground according to the standard method SCAN-C 25:76. This pulp was diluted with the ion-exchanged water according to the invention to a consistency of 0.2%, to which 0, 20 or 40%, calculated from dry pulp, of the 20% slurry of structured kaolin and acidic water (struc+AW) manufactured according to the previous example were added. In addition, for comparison of results, pulps diluted to 0.2% with pure ion-exchanged water were manufactured, to which 0, 20 or 40% of precipitated calcium carbonate, calculated from dry pulp, (PCC, Precarb FS-240, Shaefer­Finland Oy), Covergloss (Kamin L.L.C) or Alphatex (Ineryx) were added. From all of these, a 20% slurry was made in ion-exchanged water before adding it to the pulp. The test points are called struc+AW, struc, PCC, Covergloss, and Alphatex.

Regarding the abbreviations:

“Struc” refers to structured kaolin;

“PCC” refers to precipitated calcium carbonate;

“Covergloss” is a filler that contains conventional, non-structured kaolin; and

“Alphatex” is conventional, non-structured, calcined kaolin.

Slurries were manufactured from all of these either in acidic water (whereby the test point was also called by the abbreviation AW) or in pure ion-exchanged water, and this slurry was added to the paper slush, from which the pulp according to the test points was formed.

From the pulps of consistencies of 0.2% thus manufactured, sheets of 80 g/m$^2$ were produced in a sheet mould without circulated water, according to the standards SCAN-C 26:76 (SCAN-M 5:76). 10 sheets were made from each test point by using cationic polyacrylamide (Pronestret PK 435) as retention agents. 250 g/l of polyacrylamide were added by mixing without shearing forces. After this, the sheets were wet-pressed and dried in a drum drier (120°C, 2 hours), as described in the publication of Pertti Aaltosen from 1986 (Pertti Aaltosen: Kuivaukka-aineen ja paperin testausmetodit (Testing methods for fibre raw material and paper), Otakustantamo, 1986). All sheets thus manufactured were conveyed to be aerated for 48 hours at 23°C and a relative humidity of 50%. After this, the basis weights of the sheets were verified and these properties were determined.
As indicated by the results, adding the structured kaolin that was suspended in acidic water (struc+AW) to the pulp and combining the structured kaolin with the carbonate thus precipitated improve the brightness, opacity, strength, stiffness, and printability (optical density) more than the use of structured kaolin alone (struc) or the use of PCC alone (PCC). The strength (Scott bond) also increases, while the round structured kaolin of a size of about 15 micrometers weakens the formation of hydrogen bonds between the fibres less than when using the fillers of a smaller size (Covergloss, Alphatec, and PCC).

Example 3
The Effect of Conventional Kaolin Suspended in Acidic Water on the Properties of Paper

In this example, dry Intrafil C (Imerys), which is conventional kaolin, is suspended in acidic water or ion-exchanged water to a dry matter content of 20%. The acidic water used is made as in example 1.

The Valley grinder was used to first grind a mixture of bleached pine pulp and bleached birch pulp to an SR number of 3.5. The amount of pine pulp from the weight of the pulp was 30% and that of birch pulp was 70%. The pulp was ground according to the standard method SCAN-C 25:76. This pulp was diluted to a consistency of 0.2%, to which Intrafil C (Intra) that was suspended in 0, 20 or 40% of ion-exchanged water or Intrafil C (Intra+AW) that was suspended in acidic water was added.

From the pulps of consistencies of 0.2% thus manufactured, sheets of 80 g/m² were produced in a sheet mould without circulated water, according to the standards SCAN-C 26:76 (SCAN-M 5:76). 10 sheets were made from each test point using cationic polyacrylamide (Paenastar PK 435) as retention agents. 250 g/l of polyacrylamide were added by mixing without shearing forces. Thereafter, the sheets were wet-pressed and dried in a drum dryer (120°C, 2 hours).

All sheets thus made were taken to be aerated for 48 hours at 23°C and a relative humidity of 50%. After this, the basis weights of the sheets were verified and these properties were determined:

<table>
<thead>
<tr>
<th>Test point</th>
<th>Opacity, %</th>
<th>Brightness, %</th>
<th>Scott Bond, μm²</th>
<th>Stiffness, μNm</th>
<th>Optical density, 10 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covergloss</td>
<td>85.5</td>
<td>82.2</td>
<td>242</td>
<td>78</td>
<td>1.30</td>
</tr>
<tr>
<td>Alphatec</td>
<td>87.5</td>
<td>83.4</td>
<td>260</td>
<td>85</td>
<td>1.42</td>
</tr>
<tr>
<td>PCC</td>
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<td>84.5</td>
<td>267</td>
<td>68</td>
<td>1.44</td>
</tr>
<tr>
<td>Struc</td>
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<td>83.0</td>
<td>312</td>
<td>85</td>
<td>1.52</td>
</tr>
<tr>
<td>Struc+AW</td>
<td>89.2</td>
<td>85.3</td>
<td>315</td>
<td>138</td>
<td>1.56</td>
</tr>
<tr>
<td>Reliability</td>
<td>±0.4</td>
<td>±0.2</td>
<td>±1.2</td>
<td>±0.6</td>
<td>±0.00</td>
</tr>
</tbody>
</table>

As the results indicate, the opacity and brightness, in particular, do not improve as much with conventional kaolin as with structured kaolin.

While the present invention has been illustrated and described with respect to a particular embodiment thereof, it should be appreciated by those of ordinary skill in the art that various modifications to this invention may be made without departing from the spirit and scope of the present invention. What is claimed is:

1. A fibre product that contains pulp fibre or wood fibre, wherein filler particles are attached between the fibres and to the fibrils, part of them consisting of chemically structured kaolin agglomerates or granules, and part consisting of carbonate.
2. The product according to claim 1, wherein there is provided a binder between the fibres, between the fibres and filler particles, as well as between the fibrils of the fibres and the filler particles, which binder preferably is latex, silicon dioxide, soluble aluminium or aldehydes or a mixture thereof, preferably in an amount of 0.05-20% by weight.
3. The product according to claim 1, with structured kaolin particles up to 25% by weight of the fibre, preferably at least 5% by weight of the fibre.
4. The product according to claim 1, wherein the structured particles have an essentially spherical shape and a size of ≥5 μm, preferably 10-40 μm, more preferably 20-40 μm.
5. The product according to claim 1, wherein the kaolin of the structured filler is delaminated, water-washed, dry-classified, or it is treated using two or more of the said treating
methods, preferably changed by heating into metakaolin or calcined kaolin at least on the outer surfaces of the particles.

6. The product according to claim 1, wherein the salts of carbonic acid at normal pressure are carbonate or bicarbonate salts, preferably bicarbonate and colloidal carbonate, and more preferably have an average particle size of <0.3 nm, most suitably <0.1 nm.

7. The product according to claim 1, wherein the carbonate or bicarbonate salt or a mixture thereof that is formed from a corresponding oxide or hydroxide is a precipitated inorganic or organic salt or a composite or mixture of several salts, the salt preferably being a calcium or magnesium salt or a mixture thereof.

8. The product according to claim 1, further containing retention agents or flocculating or coagulating microparticles or a mixture thereof.

9. The product according to claim 1, which further contains one or more chemicals known as such, which are selected from the group of aluminum compounds, stock sizes, surface sizes, colouring agents, starches, optical brighteners, plastic pigments, natural and synthetic polymers, as well as fillers and coating agents.

10. A method of manufacturing a fibre product comprising: adding an oxide or hydroxide to an aqueous solution to form a hydroxide slurry, and reducing the pH of the solution to a range of 6.0–8.3 by conveying carbon dioxide to the solution so that the content of the salts of carbonic acid formed from the carbon dioxide and the hydroxide slurry is at least 0.01%, calculated from the total weight of the solid matter of the solution, whereby a salt composition is formed; suspending kaolin sheets or stacks or both in water together with a binder, whereby a kaolin composition is formed; producing kaolin drops in a spray drier from the kaolin composition, which is formed from the kaolin sheets or stacks or both and contains the binder, whereby excess water also evaporates, whereby structured kaolin particle are formed, or forming these structured kaolin particles by means of a mixing technique from the kaolin sheets or stacks or both, which are in the form of the slurry in the salt composition described above or its dissolved portion, with the binder, admixing the formed structured kaolin particles together with the salt composition or its dissolved portion to a paper or board pulp, whereby a fibre dispersion is formed; and precipitating the carbonate from the salt composition into particles in the dispersion while the dispersion is filtered, pressed, and dried into paper or board.

11. The method according to claim 10, wherein the aqueous solution is raw water, chemically or mechanically purified water, or water that is purified to various degrees of purity, or other kind of water used in a paper factory, or a mixture thereof, preferably filtered water or process water, from which the solid matter is separated or has been separated.

12. The method according to claim 10, wherein the used aqueous solution is chemical pulp (sulphate or sulphite pulp), mechanical or chemi-mechanical pulp, pulp manufactured with alkalis, recycled fibre, deinked fibre, nanocellulose pulp, coated reject, uncoated reject or a mixture thereof.

13. The method according to claim 10, wherein paper pulp is first manufactured from the aqueous solution, the solid matter of the paper pulp being mixed into the solution, wherein the stages are carried out.

14. The method according to claim 10, wherein the salt composition is manufactured from the carbonates or bicarbonates of magnesium or calcium, or a mixture thereof, by adding the slurry of oxide or hydroxide to the aqueous solution and conveying carbon dioxide to the solution, so that the pH in the aqueous solution remains essentially below 8.3 throughout this stage, whereby bicarbonate and colloidal carbonate are formed, their average particle size being <0.3 nm.

15. The method according to claim 10, wherein the particles of structured kaolin are granules or agglomerates, which, at least on their outer surfaces, are converted into metakaolin or calcined kaolin by heating.

16. The method according to claim 10, wherein binder is added to the kaolin slurry, mixing it at the same time, whereby the binder settles on the surface of the kaolin, particularly, on the surface of the structured particles that are formed from the kaolin.

17. The method according to claim 10, wherein one or more chemicals known as such are added to the fibre dispersion, being selected from the group of aluminium compounds, stock sizes, surface sizes, colouring agents, starches, optical brighteners, plastic pigments, natural and synthetic polymers, as well as fillers and coating agents.

18. The method according to claim 10, wherein retention agents or coagulating or flocculating microparticles or a mixture or copolymer thereof are added to the aqueous solution or fibre dispersion, in an amount of at least 0.01%, particularly about 0.01–3%, calculated from the total weight of the solid matter of the solution or dispersion.

19. The product according to claim 2, with structured kaolin particles up to 25% by weight of the fibre, preferably at least 5% by weight of the fibre.

20. The product according to claim 2, wherein the structured particles have an essentially spherical shape and a size of >5 μm, preferably 10–40 μm, more preferably 20–40 μm.