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(54) **Title**: USE OF PRECIPITATED CARBONATE IN THE MANUFACTURE OF A FIBRE PRODUCT

(57) **Abstract**: The present invention relates to a filler or a filler mixture containing carbonate, as well as to a process for manufacturing the same by precipitating the filler directly into the pulp or, as a separate process without the presence of fibres, particularly from the wire water of the paper or board manufacture. The invention also relates to a fibre product containing this filler, such as a paper or board product, or a plastic, rubber, concrete or paint product.

USE OF PRECIPITATED CARBONATE IN THE MANUFACTURE OF A FIBRE PRODUCT

Field of the invention

The present invention relates to a filler or a filler mixture, which contains carbonate, and to a process for the manufacture thereof by precipitating the filler directly into the pulp or as a separate process without the presence of fibres, particularly from the white water of the paper or board manufacture. The invention also relates to a fibre product which contains said filler, such as a paper or board product, or a plastic, rubber, concrete or paint product.

Description of the prior art

During the past decades, the demand for precipitated calcium carbonate has been growing strongly particularly in the paper and board manufacture, the processing of rubbers and plastics, and the manufacture of printing inks, paints, and adhesives. Precipitated calcium carbonates have an excellent brightness and scattering ability, as well as a low price. Furthermore, precipitated calcium carbonate can increase the mechanical strength, when used in the applications mentioned above.

These calcium carbonates have a crystal structure that typically is in the form of calcite, aragonite, or vaterite. Calcite is typically found in crystal forms, such as the scalenohedral, rhombohedral, cubic, and prismatic forms. Aragonite is orthorhombic and it is typically found in elongated forms. At normal temperature and pressure, vaterite is unstable, changing into calcite and aragonite. Generally, vaterite has a spherical shape. The crystal form can be transformed into acicular, cubic, spherical, and many other crystal forms by changing the reaction conditions, such as the concentration of the slaked lime and the reaction temperature.

The strength of paper and board mainly develops between the fibre and the charged groups of fines, due to hydrogen bonds. These charged groups particularly include hydroxyl and carboxyl groups. When improving the strength, it

is primarily done in a mechanical manner by grinding the fibres, thereby attempting to increase the fibrillation of the fibres. The strength is dependent on the strength of an individual fibre grade, the strength between the fibres, the number of fibre bonds, as well as the distribution of fibres and bonds in the finished paper or board.

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 they have a light colour. The most typical fillers include kaolins, talcs, ground calcium carbonate (GCC), and precipitated calcium carbonate (PCC). In addition, there are more expensive special pigments, such as precipitated aluminium silicates, satin white, and titanium dioxide. Drawing an exact line between fillers and coating pigments is difficult, but roughly fillers have a larger size and a coarser shape than the pigments used in coating. In theory, an optimal particle size for the most common fillers and coating pigments, from the point of view of maximum light scattering, is about 0.4 – 0.5 µm. Typically, the average particle size of coating pigments is, however, 0.5 – 1 µm, and that of fillers 1.5 – 4 µm.

The greatest disadvantage of using fillers and pigments, as well as other fillers, is the weakening of the strength of the paper or board structure when replacing particularly chemical mass with filler. This is caused by fillers preventing the generation of hydrogen bonds between the fibres by attaching themselves to the surface of the fibres. However, calcium carbonates, both the ground (GCC) and precipitated (PCC) forms, are widely used because of their low price and good light scattering properties, particularly in replacing the fibre of chemical pulp. Paper and board that is manufactured from recycled, de-inked and mechanical pulps could be replaced with calcium carbonates, but the darkening of mechanical pulp caused by alkali often limits their use in the manufacture of the paper and board grades manufactured from these pulps.

Historically, the problem of reduced strength caused by the addition of filler has been reduced particularly by agglomerating single filler particles into larger agglomerates. This has been presented, among others, in US specifications 4 225 383, 4 115 187, 4 445 970, 5 514 212, and 4 710 270, as well as GB publications

2 016 498 and 1 505 641. Typically, the anionic filler particles in these have been agglomerated into larger aggregates with a cationic additive in a mixture. It has been observed that the strength properties and filler retention have improved in this way, but at the same time, the optical properties have declined.

There are also publications, wherein latexes have been utilised to reduce the decrease in strength caused by the addition of fillers. This is presented, among others, in US specifications 4 178 205, 4 189 345, 4 187 142, 4 710 270, and 7 074 845.

The decrease in strength and stiffness of the paper or board product when the fibre is replaced with filler are mainly caused by the fillers weakening the generation of hydrogen bonds between the fibres, since the surface of the fillers does not form hydrogen bonds. At present, the filler is generally added directly to the pulp. In the wire section, only a portion of the added filler is attached to the finished paper or board web. Regardless of this, the rest of the filler is conducted through the white water system to form a 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. Generally, these runnability problems in the paper or board machine appear, for example, as contamination of the wires and felts, and finally, as breaks. A part of the filler of the white water system also finally burdens the sewage treatment plant, since all of the material is never carried out of the process along with the finished paper or board. The weaker fibre-fibre bonds on the surface of the paper or board that are caused by the filler may also result in an increase in the dust formation of the surface during printing.

Consequently, there is a need for a fibre product, wherein the filler would attach to the fibre and the other fillers more effectively and, at the same time, would provide the product with advantageous strength properties that preferably would be further improved in comparison with the known solutions.

Brief description of the invention

An object of the present invention is to provide a new fibre product, such as a paper or board product, which has a high strength, brightness, ink density, and opacity.

Particularly, it is an object of the present invention to provide a new carbonate-containing filler that can be utilised in such a fibre product, especially so that the carbonate filler is attached to the gaps between the fibres of the fibre product.

Such a carbonate-containing filler and fibre product can be provided, for example, by the process according to the invention.

The present invention thus relates to the carbonate-containing filler and to the production process of the same. Such a filler is further utilised in the process of manufacturing the fibre product according to the invention, wherein the fibre product contains chemical pulp fibre and/or wood fibre and/or synthetic fibre, and which preferably is paper or board. In this process of manufacturing the fibre product, carbonate filler is attached between the chemical pulp fibres or wood fibres and to the fibrils, whereafter said fibre product is produced from the pulp.

More precisely, the process of manufacturing the carbonate-containing filler according to the present invention is characterised by what is stated in the characterizing part of claim 1.

The carbonate-containing filler or filler mixture according to the invention, in turn, is characterised by what is stated in the characterizing part of claim 9.

Correspondingly, the process of manufacturing the fibre product according to the invention is characterised by what is stated in the characterizing part of Claim 14, and the use of the filler according to the invention is characterised by what is stated in Claim 18.

Several considerable advantages are reached using the invention. It has been demonstrated that by using underpressure when forming the carbonate-containing filler, improvements are achieved in the brightness, strength, opacity, and printability (the absorption properties of the ink) of the final product, such as the paper or board, which utilizes the carbonate. Thus, a part of the fibres of the final product can be replaced with the filler so that the strength properties simultaneously are maintained on a better level than when using conventional fillers.

Particularly advantageous properties are achieved when a polymer that increases the dry strength is used together with the carbonate in the filler or with the filler in the manufacture of the fibre product.

To increase the pH and form the carbonate in negative pressurisation, it is sufficient to release the carbon dioxide from the reaction mixture without adding a separate chemical, i.e. alkali. This is of particular advantage at the paper and board mills, where there is a capacity of free carbon dioxide available from the pulp mill.

Brief description of the drawings

Fig. 1 is a graphic depiction of the impact of the particle size of the carbonate filler (APS) and a portion of starch on the TEA values (TEA1) of the fibre product, when a basis weight of 80 g/m^2 and 10% of carbonate filler are used in the fibre network.

Fig. 2 is a graphic depiction of the impact of the particle size of the carbonate filler (APS) and a portion of starch on the Scott Bond values (Scott1) of the fibre product, when a basis weight of 80 g/m^2 and 10% of carbonate filler are used in the fibre network.

Fig. 3 is a graphic depiction of the brightness and opacity values of kaolins and the carbonate filler (a size category of 6.5 μm). The results are normalized to a filler content of 6% in a basis weight of 80 g/m^2.

Fig. 4 shows scanning electron microscope images of chemical pulp sheets of 80 g/m^2, comprising carbonate fillers of a size category of 13 μm (the upper row) and 6.5 μm (the lower row) on the surface of the sheets.

Detailed description of the preferred embodiments of the invention

In the commonly used precipitation processes of carbonate, the precipitated calcium carbonate (PCC) is manufactured by changing the pH from alkaline toward neutral. In the manufacture of the carbonate filler according to the present invention, the pH is increased from acidic to a pH of over 7. The purpose is to provide carbonate at the precipitation stage, which together with possible polymers increasing the dry strength could increase the strength of the filler-containing network in the final product, without weakening the optical properties (opacity and brightness).

The present invention thus relates to a process of manufacturing a filler containing carbonate, wherein an acidic bicarbonate ion solution is formed from a corresponding hydroxide solution by adding carbon dioxide to said hydroxide solution, whereafter the carbonate portion of the filler is formed by increasing the pH of the formed acidic bicarbonate ion solution to a neutral or alkaline range by means of underpressure or centrifugal force or a combination thereof.

“Acidic” in this context refers to a pH value of below 7, whereas “neutral” refers to a pH value within 7 – 8, and “alkaline” refers to a pH value of over 8, particularly over 10.

“Underpressure or negative pressure” in this context refers to a pressure under ambient pressure or air pressure, preferably within the range of 0.60 – 1 bar, i.e. as an absolute pressure 0.4 – 0 bar; more preferably within the range of 0.85 – 0.95 bar, i.e. as an absolute pressure 0.15 – 0.05 bar; particularly within the range of 0.88 – 0.94 bar, i.e. as an absolute pressure 0.12 – 0.06 bar.

When exploiting centrifugal force, a speed of rotation of 50 – 2000 rpm (rotations per minute) is preferably used.

The temperature while carrying out the stages of the process can be close to ambient temperature (about 25°C) or slightly higher, particularly 35 – 70 °C.

The used hydroxide is preferably calcium hydroxide or magnesium hydroxide or a mixture thereof. More preferably the used hydroxide is manufactured by elutriating burnt lime, burnt dolomite, MgO or another source of calcium or magnesium in water or an aqueous solution, which when elutriated in such a solution gives an alkaline solution, or by elutriating a mixture of two or more of the above.

The hydroxide and the carbon dioxide can be added to said aqueous solution essentially at the same time. Optionally, they are added at different stages.

The "aqueous solution" refers to all solutions or suspensions which contain more than 50% by weight of water. Consequently, the aqueous solutions include both pure water (100% by weight of water) and dilute fibre suspensions.

Any of the aqueous solutions of the paper or board machine can be converted into the bicarbonate ion solution suitable for use as the starting material solution of the process. Preferably, said aqueous solution is a process water of the paper or board manufacture, particularly circulation water.

A "bicarbonate ion solution", in turn, is an aqueous solution containing various states of carbonate, its pH being within a range where the states of carbonate are presumably mainly in the form of bicarbonate; in this connection particularly in a pH range of 4 – 10.

When varying the pH of the carbonate- or bicarbonate-containing solution, e.g. according to the invention, its carbonate states also vary according to the so-called carbonate system. The main states of the carbonates are:

$$H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$$

At an acidic pH, soluble carbon dioxide (CO_2) and, to a minor extent, carbonic acid (H_2CO_3), are the main states of carbonate. In the neutral (on both sides of a pH of 7) and alkaline ranges, bicarbonate or hydrogen carbonate (HCO_3^-) is the main state of carbonate up to a pH of about 10. In a highly alkaline range (pH > 10), carbonate (CO_3^{2-}) is the main state.

The alkalinity of carbonate refers to the content of strong acid, with which the aqueous solution can be titrated to the end point of phenolphthalein. At this point, all of the CO_3^{2-} has been converted into the ion state HCO_3^-. This takes place at a pH of about 8.3. In the most important pH range of the paper and board manufacture, pH 6–8, bicarbonate (HCO_3^-) is the predominant state. Further, reasonably well dissolved carbon dioxide and some carbonic acid and colloidal carbonate have entered this pH range from the acidic side of the pH range.

The solution in the acidic pH range (pH < 6) is herein called the acidic bicarbonate ion solution.

In the present invention, carbonate is formed from the bicarbonate ions in the solution. It is common knowledge that bicarbonate ions can be precipitated into carbonate particles from a carbonate ion solution by increasing the pH or the temperature.

When the temperature is increased, carbon dioxide is released and the bicarbonate reacts with, e.g., free calcium or magnesium ions, according to the following reaction equation:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O\uparrow.$$

Correspondingly, 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:

$$Ca^{2+} + 2HCO_3^- + 2NaOH \rightarrow CaCO_3\downarrow + Na_2CO_3 + 2H_2O.$$

$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2OH^-$.

However, the present invention is based on a situation where sufficiently warm bicarbonate ion solution (of at least room temperature) is subjected to underpressure or the effect of centrifugal force, so that carbon dioxide is released to the air from the solution.

In particular, it has been demonstrated that improvements are achieved in the strength, opacity, and printability (the absorption properties of the ink) of the final product, such as the paper or board, in this manufacture of carbonate filler by using underpressure, for example directly in the process of the paper or board mill. These advantages are further enhanced when the polymer that increases the dry strength is used with the carbonate in the filler, or in the final product that is manufactured with the filler.

To increase the pH and form the carbonate in under-pressurisation, it is sufficient that the carbon dioxide is released from the bicarbonate ion solution described above, which is at an acidic pH, without a separate chemical, such as alkali. This is of particular advantage in the paper and board mills, where there is a free carbon dioxide capacity available from a pulp mill for the manufacture of the acidic bicarbonate ion solution.

In the paper and board industry, calcium carbonate is commonly used as the carbonate, both as a filler and as a coating pigment. Well-known forms of calcium carbonate include ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). Conventionally, the aim has been to keep their average particle size as larger than 500 nm, typically 1 – 2 µm, as it is believed that the best possible light scattering efficiency (brightness and opacity) is then achieved. Their solubility in water is fairly low under normal conditions. However, under acidic conditions soluble calcium ions are released, increasing the hardness of the water.

The average particle size (APS50) of the carbonate manufactured according to the present invention is preferably 0.5 – 15 µm, particularly 1 – 8 µm.

Further filler can be added to the acidic bicarbonate ion solution used in the invention before the carbonate portion of the filler is formed from the solution. This added filler is preferably commercial GCC or PCC or a mixture thereof or, optionally, a filler other than carbonate, such as wollastonite, aluminium silicate, kaolin, talc, satin white or a titanium oxide.

The "carbonate portion" in this context refers to the solid carbonate of the filler or filler mixture which is to be formed or is formed online, thus describing the carbonate content in comparison with the added fillers or corresponding additives. This portion is preferably > 5%.

It is also possible to increase the dry matter content of the obtained filler solution containing carbonate. This is carried out, particularly, by infiltrating, depositing, pressing, evaporating, drying, or by means of centrifugal force.

According to an embodiment of the invention, a dry strength polymer is used with the carbonate portion of the filler, preferably being selected from the group of starch, aldehyde starch, guar gum, polyacrylamide, glyoxilized polyacrylamide, carboxyl methyl cellulose, polyvinyl alcohol, latex or citosane, or a mixture of two or more of the above, most preferably from a starch.

In the paper or board industry, the decrease in dry strength caused by the use of fillers has typically been compensated using water-soluble natural and artificial polymers. The use of fillers increases the need to use dry strength agents. The most typical dry strength agents include starch, carboxyl methyl cellulose (CMC), guar gum, and polyacrylamide (PAM). Polyvinyl alcohol and latex can also be used as dry strength polymers, even though in practice, they are generally not used in the wet section of the paper or board manufacturing process.

Starch is the oldest and most commonly used dry strength agent in increasing the strength of fibre networks, its strength-increasing impact being caused by its large amount of hydroxyl groups, which increase the generation of hydrogen bonds. Cationic and amphoteric starches are the most commonly used starches. Generally, when these are added to high consistency pulp, the effect is primarily

an increase in the strength properties. In addition to cationization, an ether bond can be formed in the starch in the manufacture of carboxyl methyl cellulose (CMC). Native starch can further be esterified, oxidized, hydrolyzed, and treated using a combination of enzymes and heating or some or all of the above. The most typical sources of native starch are potato, barley, wheat, corn and tapioca. However, when added to a dilute pulp or short circulation pulp, the starch improves the retention of the fines and filler, instead of increasing the strength.

In addition, starch is used in the dispersion of stock sizes, such as AKD and ASA. The surface sizing of paper is also often carried out with starch, as well as the attachment of the various layers of board to each other.

According to a particularly preferred embodiment, the carbonate filler is manufactured so that the aqueous solution is first rendered acidic by dosing carbon dioxide into it either simultaneously or before burnt lime or dolomite or the corresponding hydroxide solutions thereof is/are added to the aqueous solution. The bicarbonate ion solution according to the invention, which has been acidified, is then obtained. Subsequently, the pH of the solution is increased to the neutral or alkaline range by under-pressurisation, whereby the carbonate filler according to the invention is generated.

The present invention also relates to the filler or filler mixture containing carbonate which has been manufactured by means of the above-described process. The filler or filler mixture in question is thus manufactured by a process, wherein the pH is increased by means of underpressure or centrifugal force or a combination thereof from the acidic range to the neutral or alkaline region.

This filler contains at least 5% by weight, preferably 25 – 100% by weight, most suitably 50 – 90% by weight of carbonate, which has been formed in solid form in the aqueous solution. The average particle size of this carbonate is preferably 0.5 – 15 µm, particularly 1 – 8 µm. The carbonate is preferably selected from calcium or magnesium carbonate or a mixture thereof. Most suitably, the filler consists of this calcium or magnesium carbonate or a mixture thereof. Particularly preferred

fillers in the connection of the invention are ground calcium carbonate (GCC), precipitated calcium carbonate (PCC) or mixtures thereof.

The pH of the filler formed according to the invention is neutral or alkaline. The final pH value of the filler is preferably 6 – 8.

The carbonate manufactured online, according to the invention, can also be mixed with the additional filler into a filler mixture. This added filler is preferably commercial GCC or PCC or a mixture thereof, or, optionally, it contains a filler other than a carbonate, such as wollastonite, aluminium silicate, kaolin, talc, satin white or a titanium oxide.

According to an embodiment of the invention, the carbonate portion of the filler is in the final filler already mixed with the dry strength polymer, most preferably in the pulp, which polymer preferably is selected from the group of starch, aldehyde starch, guar gum, polyacrylamide, glyoxilized polyacrylamide, carboxy-methyl cellulose, polyvinyl alcohol, latex or citosane, or a mixture of two or more of the above, most preferably from a starch.

The present invention further relates to a process of manufacturing a fibre product containing chemical pulp fibre, wood fibre or synthetic fibre, or a mixture thereof. In this process, the pulp is manufactured, to which the carbonate-containing filler is added, whereafter the pulp is compressed into a fibre product, which optionally is coated.

The used filler or filler mixture increases the optical properties of the structure of the fibre product to be manufactured, and maintains its strength properties, optionally together with the water-soluble, dry strength -increasing polymer.

The fibre product refers to a thin, plate-like fibre product, which particularly is a paper or board product.

The fibres of the product can be any natural fibres or synthetic fibres or a mixture thereof. In particular, the fibres can be chemical pulp or mechanical pulp or a

mixture thereof. For example, sulphate and sulphite cellulose fibres, dissolving pulp, nanocellulose, chemi-mechanical (CTMP), thermomechanical pressure groundwood (TMP), pressure groundwood (PGW), groundwood pulp, recycled fibre, or fibres of de-inked pulp can constitute the fibres of the product. Typically, sulphate and sulphite celluloses are called chemical pulps, and thermo-mechanical pulp, pressure groundwood, and groundwood pulp are called mechanical pulps. The density of pulp made from these fibres, when the filler or filler mixture according to the invention is added thereto, is preferably 0.1 – 5%, particularly 0.2 – 1.5%.

In the paper or board manufacturing process, a "filler" specifically refers to the particles, which are added or attached to the gaps between the fibres, and the purpose of which is to reduce the fibre content of the final product. In connection with the present invention, the definition also covers pigments, including coating pigments.

Typically, such known fillers and pigments of the paper and board manufacture have an average particle size of less than 5 µm, and they have a light colour. The most typical fillers include kaolins, talcs, ground calcium carbonate (GCC), and precipitated calcium carbonate (PCC). In addition, there are more expensive special pigments, such as precipitated aluminium silicates, satin white, and titanium dioxide. Drawing an exact line between fillers and coating pigments is difficult, but roughly, fillers have a larger size and a coarser shape than the pigments used in coating. In theory, an optimal particle size for the most common fillers and coating pigments, from the point of view of maximum light scattering, is about 0.4 – 0.5 µm. Typically, the average particle size of coating pigments is, however, 0.5 – 1 µm, and that of fillers 1.5 – 4 µm.

According to the invention, at least the carbonate portion of the filler used in the fibre product is formed in the aqueous solution to be used in the manufacture of the pulp before the pulp is compressed into the fibre product, or it is formed in a coating paste before the optional coating of the fibre product. Thus, when the fibre product is a paper or board product, the aqueous solution, in which the carbonate

portion is formed, is then the process water of the paper or board manufacture, preferably the circulation water, particularly before the head box of the machine.

To prepare the carbonate of the filler, the above-described process is used, wherein the pH is increased from the acidic range to the neutral or alkaline range by means of under-pressure or centrifugal force or a combination thereof.

The carbonate to be formed is preferably calcium or magnesium carbonate or a mixture thereof.

It is also possible to increase the dry matter content of the filler solution containing carbonate before adding it to the fibres. Particularly, this is carried out by infiltrating, depositing, pressing, evaporating, drying, or by means of centrifugal force.

According to an embodiment of the invention, a dry strength polymer is used in the pulp with the carbonate portion of the filler, preferably selected from the group of starch, aldehyde starch, guar gum, polyacrylamide, glyoxilized polyacrylamide, carboxyl methyl cellulose, polyvinyl alcohol, latex or citosane, or a mixture of two or more of the above, most suitably from a starch.

In the present invention, the amount of optionally used starch is 0 – 40 kg/t of pulp. Increasing the addition from this limit weakens among others the dewatering of the wire section. This is caused by the anionic charge of the fibres and the filler being neutralized by the cationic starch, whereby the rest of the starch no longer attaches to the fibres and the filler, but remains in the form of dissolved starch in the circulation waters.

The following non-limiting examples illustrate the invention and its advantages.

Examples

The following examples illustrate the improvements in several properties of paper technology, which are achieved by means of the carbonate filler according to the invention.

In theory, it could be considered that the structure of the fibre product manufactured according to the invention would improve the opacity and printability of the product, when the carbonate filler that is brighter than the fibres is incorporated into the fibre network. This improves the light scattering and the absorption of ink.

The increase in strength properties with the same filler and filler content is due to the carbonate filler still being in an unstable, amorphous state when brought together with the fibres, whereby the carbonate filler is capable of increasing the strength bonds between the hydroxyl groups of the dry strength polymer and the hydrogen-bonding groups of the fibre.

Example 1 (Manufacture of the acidic bicarbonate solution)

The acidic bicarbonate ion solution was manufactured by mixing 100 or 200 g of burnt lime (CaO) with 500 g or 1000 g, respectively, of water at 45 °C. The $Ca(OH)_2$ slurry thus generated was added to 30 litres of tap water. Subsequently, the water and the calcium hydroxide were allowed to react with carbon dioxide conveyed to the mixture, so that the pH of the mixture at the end of the reaction was 6.3. After 12 hours of sedimentation, the precipitate that sedimented on the bottom was separated from the dissolved and colloidal material (Ca ions, carbonic acid, bicarbonate and colloidal calcium carbonate). The precipitate that sedimented on the bottom was not used in the tests. The bicarbonate ion solution thus manufactured was used as raw material in the precipitation tests described below.

A portion of the acidic bicarbonate ion solutions thus manufactured was further utilised, so that their entire solid matter (also the sedimenting portion) was heated

to 50 °C and underpressurised for 5 minutes to 0.92 bar, i.e. 0.08 bar absolute pressure. The underpressurization was carried out in a 50-litre steel container. The underpressure was created by means of a pump. As a result, the particle sizes (APS10, APS50, and APS90), conductivity, and pH of Table 1 were obtained.

Table 1. 100 and 200 g of CaO per 30 litres of water. All of the solid matter was underpressurised.

gCaO/30L	APS10, µm	APS50, µm	APS90, µm	Conductivity, µS/cm	pH
100	2.8	8.5	28.5	460	7.5
200	1.3	6.2	13.8	450	7.5

In the above table 1, the 100 g of CaO in 30 litres contained 5.6 g/l of carbonate after the underpressurisation. The 200 g of CaO in 30 litres contained 11.3 g/l of carbonate after the underpressurisation.

Example 2 (Precipitation of bicarbonate as a separate process)

In this example, the bicarbonate ion solutions (30 litres) manufactured according to the previous example were used, 100 g of calcium oxide having been added to one of them and 200 g of calcium oxide to the other. The precipitate that sedimented on the bottom was not used in the tests. The bicarbonate solutions were heated to 55 °C, after which an underpressure of 0.92 bar (i.e. an absolute pressure of 0.08 bar) was allowed to influence the bicarbonate ion solution in a 50-litre steel container. The underpressure was created by means of a pump.

Tables 2 and 3 show the delay times, after which the samples were taken out of the underpressure container, and the measured properties of the samples.

Table 2. 100 g of calcium oxide (CaO) per 30 litres of water.

Time, sec	APS10, µm	APS50, µm	APS90, µm	Conductivity, (µS/cm	pH
0	1.1	8.3	31.0	1430	6.63

30	3.3	5.7	10.5	970	7.29
120	4.3	8.8	22.3	830	7.31
240	4.2	9.4	23.0	676	7.40
600	3.7	7.6	16.4	550	7.40

Table 3. 200 g of calcium oxide (CaO) per 30 litres of water.

Time, sec	APS10, µm	APS50, µm	APS90, µm	Conductivity, µS/cm	pH
0	2.3	11.0	28.2	1115	6.55
30	0.8	7.2	18.3	790	7.26
120	1.0	7.6	18.2	740	7.27
240	1.0	6.7	16.3	740	7.34
600	3.3	13.2	26.0	690	7.43

The above Tables 2 and 3 show that 100 g of CaO/30 l, which is at an underpressure for 30 seconds, produces the smallest average particle size (APS50). 200 g of CaO/30 l, at the underpressure for 600 sec, provides the largest carbonate particles as the average particle size (APS50). The particle sizes (APS10, APS50, and APS90) were measured with a Malvern Mastersizer 2000. Both tables indicate that along with the carbon dioxide releasing from the bicarbonate solutions, the acidic solutions become neutral and alkaline. While the pH increases at an underpressure, the conductivity decreases when the calcium ions precipitate carbonate particles from the carbonate ions.

Example 3 (Precipitation of bicarbonate with fibres present)

In laboratory tests, pine pulp and birch pulp ground to an SR number of 30 were used. Of the pulp, 70% was pine pulp and 30% was birch pulp. The density of the pulp was 3.8%. From this pulp, sheets of 80 g/m^2 were made by a sheet mould at a density of about 0.2%. Control samples were diluted to a density of 0.2% with tap water. A dilution to a density of 0.2% was made with said bicarbonate ion solution (Table 3) at the test points, in some of which a carbonate filler of 6.5 µm

or 13 µm was formed. In the following results, the filler contents are normalized to a level of 6%, if not separately otherwise stated. The control test points were:

Capim SBF, Imerys (and 10 kg/t of starch, added to the 3.8% pulp), hereinafter Capim

Intramax, Imerys (and 10 kg/t of starch, added to the 3.8% pulp), hereinafter Intramax

Control 1, i.e. sheets made from chemical pulp fibre without starch

Control 2, i.e. 5 kg/t of starch, added to the 3.8% pulp

Control 3, i.e. 10 kg/t of starch, added to the 3.8% pulp

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 from each test point). After this, the sheets were dried in a drum drier at 105 °C for two hours, before they were taken to be aerated at 23 °C and a relative humidity of 50% for 48 hours. After this, their basis weights were verified and the following properties were determined:

- Filler content (525 °C and 2 hours)
- ISO brightness (L&W Elrepho Spectrophotometer SE070), ISO 2470
- Opacity (L&W Elrepho Spectrophotometer SE070), ISO 2471
- Scott bond (Internal bond tester Huygen), TAPPI-UM403
- TEA (L&W Tensile Tester with Fracture Toughness), SCAN-P 38:80

Between the particle size of the carbonate filler manufactured at the underpressure and the portion of pulp starch, a factorial test according to a test plan was conducted, the variables being the following:

- Portion of pulp starch 0, 5, and 10 kg/t
- Average particle size (APS) of the carbonate filler 0, 6.5, and 13 µm.

For the midpoint of the test, i.e. 5 kg/t of starch and the particle size (APS) of the 6.5 micrometer carbonate filler, two repetitions were conducted to clarify statistical reliability. The underpressure conditions used for the particle size were selected according to the previous Example 2. In practice, the delay time of the underpressure is used to influence the particle size (APS) of the carbonate filler. In the test, 0 micrometers means that no carbonate filler is manufactured in the pulp. The carbonate filler sizes of 6.5 and 13 micrometers correspond to the delays of 40 seconds (100 g CaO/30 l), 6.5 µm and 600 seconds (200 g CaO/30 l), 13 µm at an underpressure of 0.92 bar and a temperature of 45 °, respectively.

To produce the underpressure, a 50-litre steel container was used, in which the underpressure was formed by means of a pump. The 3.8% pulp, to which the desired portion of starch was added, was diluted to a consistency of 0.2% with the bicarbonate ion solution, according to Example 1, before the underpressure treatment.

The cationic pulp starch used in the tests was from Chemigate Oy (Raisamyl, the DS of which was 0.035). Every time when used, the pulp starch was added to the 3.8% pulp at a mixing time of 1 minute before diluting it to a consistency of 0.2%. Kaolins (Capim and Intramax) were added to the 0.2% pulp. The bicarbonate ion solutions manufactured according to Example 1 were used for the dilution of the pulp from 3.8% to 0.2%. The carbonate fillers were manufactured from this by underpressurisation. As a retention agent, 200 g/t of PAM (Fennopol 3400, Kemira) were added to the sheet mould during the mixing.

The test points of the test plan are presented in Table 4.

Table 4. Conditions of the test plan. Starch was added to the 3.8% pulp before diluting it to 0.2%.

TEST	Starch, kg/t	The particle size of carbonate, µm	gCaO/30l	Underpressure, bar	Temperature, °C
1	0	0	0	not used	not used
2	10	13	200	0.92	45

3	5	6.5	100	0.92	45
4	0	13	200	0.92	45
5	5	6.5	100	0.92	45
6	10	0	0	not used	not used
7	5	6.5	100	0.92	45

As a whole, the test plan is extremely successful. The index of determination for the final model is over 95%. The strength was measured both as Scott Bond and TEA values. The optical values measured included opacity and brightness (ISO). Naturally, the strength (Scott & TEA) is influenced by the portion of pulp starch – 10 kg/t yields the best strength levels. The particle size (APS) of the carbonate filler as such, but especially together with the starch portion, has an obvious mutual effect on the strength. This means that the carbonate filler can be used to positively influence the reduction of the starch portion and the maintenance of strength, even though the amount of filler in the network is increased.

Fig. 1 shows that the best TEA strength is achieved, when the particle size of the carbonate filler is about 6.5 micrometers and the amount of pulp starch is 5 kg/t. The corresponding TEA strengths, J/m^2, achieved at the control points were:

Control 1	54
Control 2	70
Control 3	90.

Fig. 2 shows that the starch portion of 10 kg/t and no carbonate filler yields the best Scott Bond strength. The corresponding Scott Bond strengths, J/m^2, achieved at the control points were:

Control 1	214
Control 2	302
Control 3	324.

The strengths achieved with Capim SBF, Intramax, and the carbonate filler according to the invention, with a basis weight of 80 g/m^2 and a filler content of 10% are shown in Table 5.

Table 5. The kaolins and carbonate filler used yielded these TEA and Scott Bond values. With the kaolins, 10 kg/t, and the carbonate filler (APS 6.5 μm), 5 kg/t of pulp starch.

Filler	TEA, J/m2	Scott Bond, J/m2
Intramax	44	211
Capim	46	208
Carbonate filler	77	273

As stated above, the above values are achieved using 10 kg/t of pulp starch. When using the carbonate filler of 6.5 μm and 5 kg/t of pulp starch, a Scott Bond strength of 273 J/m^2 and a TEA strength of 77 J/m^2 are achieved. Both values are clearly higher than with the corresponding amounts of kaolin filler (Table 5). 5 kg/t of pulp starch from the pulp without the filler yielded a Scott Bond strength of 302 J/m^2, so the decrease in the maximum strength caused by the carbonate filler with this amount of starch is minor.

Between the starch portion and the particle size of the carbonate filler, there is a strong mutual impact on the strengths. The P value of the test plan for the mutual effect was 0.01. A P value lower than 0.05 means that the starch portion and the particle size of the carbonate filler have a strong mutual effect on the strengths. In terms of statistics alone, the starch portion and the particle size of the carbonate filler have a significant effect on the strengths.

Using the carbonate filler, an improved combination of opacity and brightness can be achieved, in comparison with either one of the kaolins, as indicated in Figure 3. When the results of Table 5 for kaolin and the improved strength properties with a 50% smaller amount of pulp starch obtained from the test plan are added to this, it is obvious that the carbonate filler alone, and especially with the starch, offers the

paper or board manufacturer an opportunity to achieve, with the fillers, excellent optical properties, while maintaining the improved strength properties.

Fig. 4 shows the carbonate particles of each size category, both 6.5 and 13 μm, on the surface of the manufactured chemical pulp sheets of 80 g/m^2. In the figures, one can observe the angular shape of the carbonate fillers. In the carbonate fillers of 6.5 μm in the lower row, one can also observe porosity in the structure of the carbonate filler. Fig. 4 also shows how the carbonate fillers are clearly bonded to the fibrous substance (starch and/or fibrils of the fibre).

Example 4 (Precipitation of bicarbonate with another mineral filler)

In this test series, 0, 10% and 20% of ground calcium carbonate GCC, calculated from dry fibre, was added to the 3.8% pulp of the preceding example as a control sample (Hydrocarb 60 Filler LV, Omya). As a control sample, precipitated calcium carbonate PCC (FS-240, Shaefer Finland Oy) was also used. The optical (brightness and opacity) properties and strength (Scott Bond) obtained from the control samples were compared to the results manufactured according to the preceding example and obtained using underpressure. In this example, the underpressurisations were carried out as follows: First, 5 kg/t of starch (Raisamyl DS 0.035; Chemigate Oy) was added to the 3.8% pulp. After this, the 3.8% pulp was diluted to a consistency of 0.2% with the bicarbonate ion solution and, subsequently, 10% or 20% of either GCC or PCC was added to this diluted pulp, while evenly agitating, before the underpressurisation. These test points are called GCC and PCC underpressurisations in Table 5, where the results normalized to a filler content of 5% are shown. The bicarbonate ion solution was manufactured according to Example 1 by adding 100 g of calcium oxide to 30 litres of the manufactured solution. The 0.2% fibre pulp and either 10% or 20% of GCC or PCC, diluted with the bicarbonate ion solution used, were conducted to the underpressurisation. Thereafter, this mixture was kept at an underpressure of 0.92 bar for 40 seconds. At the control points (GCC and PCC), 5 kg/t of starch was also added to the 3.8% pulp. After this, the pulp was diluted to a consistency of 0.2% with tap water. 10% or 20% of GCC or PCC was added to this diluted pulp before

making the sheets. As a retention agent, 200 g/t of PAM (Fennopol 3400, Kemira) was added to the sheet mould during the mixing.

From the pulps of consistencies of about 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 from each test point). Subsequently, the sheets were dried in a drum drier at 105 °C for two hours, before they were taken to aerate at 23 °C and a relative humidity of 50% for 48 hours. After this, their basis weights were verified and the following properties were determined:

- Filler content (525 °C and 2 hours)
- ISO brightness (L&W Elrepho Spectrophotometer SE070), ISO 2470
- Opacity (L&W Elrepho Spectrophotometer SE070), ISO 2471
- Scott bond (Internal bond tester Huygen), Tappi-UM403
- Thickness (L&W Thickness tester SE51), ISO 534

The basis weights of the sheets were at the target basis weight of 80 g/m^2, with an accuracy of ±0.6 g/m^2.

The assessment of the printing properties of the sheets in this test was made by measuring the density. The sheets were printed by the Universial Testprinter (Testprint B.V.) by using a Cold set black (Sun Chemical, viscosity 7.3 Pas) with 10 milligrams of ink on the upper surface of the sheet. The densities were measured by a densitometer (Macbeth) from the aerated and dried samples after 24 hours from the printing. The Universial testprinter employed a pressure of 630 N and a velocity of 1 m/s.

According to the filler content determined from the sheets (525°C and 2 hours), the results are normalized to the same filler content of 5%. In Table 6, the results are shown, normalized to a filler content of 5%. 95% means a confidence interval of 95%.

Table 6. The test results which are normalized to a filler content of 5% in a basis weight of 80 g/m^2.

Test point	Opacity, %	Brightness, %	Scott Bond, J/m2	Thickness, µm	Optical density, 10g
GCC	83.2	84.7	185	163	1.43
PCC	84.6	85.5	182	186	1.46
GCC underpressurisation	86.4	88.1	255	229	1.72
PCC underpressurisation	86.2	88.3	246	226	1.69
95 %	±0.5	±0.3	±9	±8	±0.06

The results of Table 6 indicate that both the strength (Scott Bond), optical values (brightness and opacity), thickness, and optical density are on an improved level at both the GCC and PCC underpressurisation points and at the control points GCC and PCC.

CLAIMS:

1. A process for manufacturing a filler containing carbonate, **characterized** by
   - forming an acidic bicarbonate ion solution from a corresponding hydroxide solution by adding carbon dioxide to the solution, and
   - forming a carbonate portion of the filler by increasing the pH of the obtained acidic bicarbonate ion solution to a neutral or alkaline range by means of underpressure or centrifugal force or a combination thereof.

2. The process according to claim 1, wherein calcium hydroxide or magnesium hydroxide or a mixture thereof is used as the hydroxide.

3. The process according to claim 2, wherein calcium, sodium, or magnesium hydroxide is manufactured by elutriating burnt lime, burnt dolomite, MgO, or another such source of calcium, sodium or magnesium in water, which when elutriated in water gives an alkaline solution, or by elutriating a mixture of two or more of the above.

4. The process according to any preceding claim, wherein the hydroxide and the carbon dioxide are added essentially at the same time.

5. The process according to any of claims 1 – 3, wherein carbon dioxide is added to the finished hydroxide solution at a separate stage.

6. The process according to any preceding claim, wherein an additional mineral-rich filler, such as GCC, PCC, wollastonite, kaolin, talc, chalk, satin white, or a mixture thereof, is added to the acidic bicarbonate ion solution before the carbonate portion of the filler is formed from the solution.

7. The process according to any preceding claim, wherein the dry matter of the obtained carbonate filler is increased by infiltrating, depositing, pressing, evaporating, drying, or by means of centrifugal force.

8. The process according to any preceding claim, wherein the hydroxide solution is selected from such aqueous solutions or aqueous pulps, which belong to the aggregates or process waters of the manufacturing process of a fibre product containing chemical pulp fibre, wood fibre, or synthetic fibre or a mixture thereof.

9. A filler or filler mixture, which contains carbonate, **characterized** in that at least its carbonate portion is manufactured by a process according to any of claims 1 – 8.

10. The filler according to claim 9, which contains calcium, sodium or magnesium carbonate, or a mixture thereof, and, preferably, consists of calcium, sodium, or magnesium carbonate or a mixture thereof.

11. The filler according to claim 9 or 10, which contains, as the carbonate portion, ground calcium carbonate (GCC), precipitated calcium carbonate (PCC) or a mixture thereof and, optionally, wollastonite.

12. The filler according to any of claims 9 – 11, which is admixed to a dry strength polymer, which preferably is selected from the group of starch, aldehyde starch, guar gum, polyacrylamide, glyoxilized polyacrylamide, carboxyl methyl cellulose, polyvinyl alcohol, latex or citosane, or a mixture of two or more of the above, most suitably from a starch.

13. The filler according to any of claims 9 – 12, which is at a neutral or alkaline pH.

14. A process for manufacturing a fibre product containing chemical pulp fibre, wood fibre or synthetic fibre, or a mixture thereof, wherein a fibre pulp is manufactured, wherein a carbonate-containing filler is used, whereafter the fibre product is compressed from the pulp and optionally coated, **characterised** in that at least the carbonate portion of the used filler is formed in an aqueous solution used for the manufacture of the pulp, before the pulp is compressed into the fibre product, or it is formed in a coating mix before the optional coating of the fibre product, by using the process according to any of claims 1 – 8.

15. The process according to claim 14, wherein GCC or PCC or a mixture thereof is used as the carbonate portion of the filler or a part thereof, and wherein the filler can also contain wollastonite.

16. The process according to claim 14 or 15, wherein at least the carbonate portion of the filler is formed into the aqueous solution before the head box of the machine used in the manufacture of the fibre product.

17. The process according to any of claims 14 – 16, wherein a paper or board product is manufactured.

18. Use of the filler according to any of claims 9 – 13 in plastic, concrete, rubber, or paint.

Fig. 1

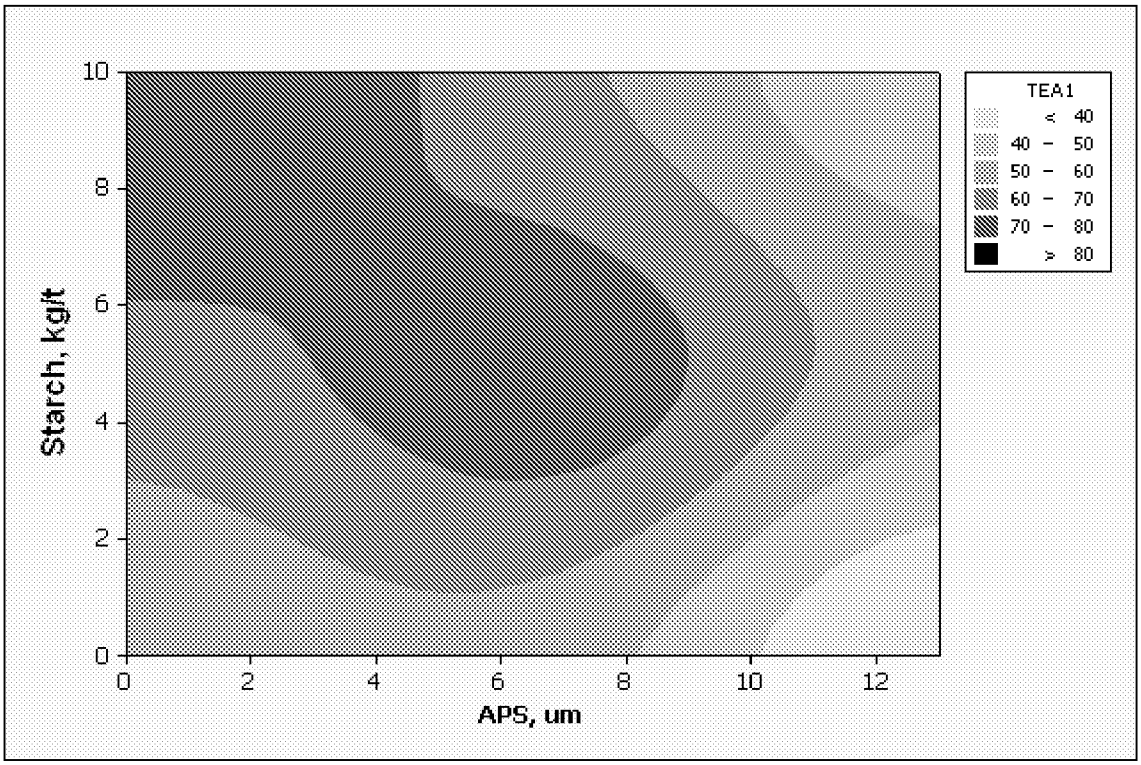

TEA1
≤ 40
40 – 50
50 – 60
60 – 70
70 – 80
> 80
Starch, kg/t
APS, um
0
2
4
6
8
10
12

Fig. 2

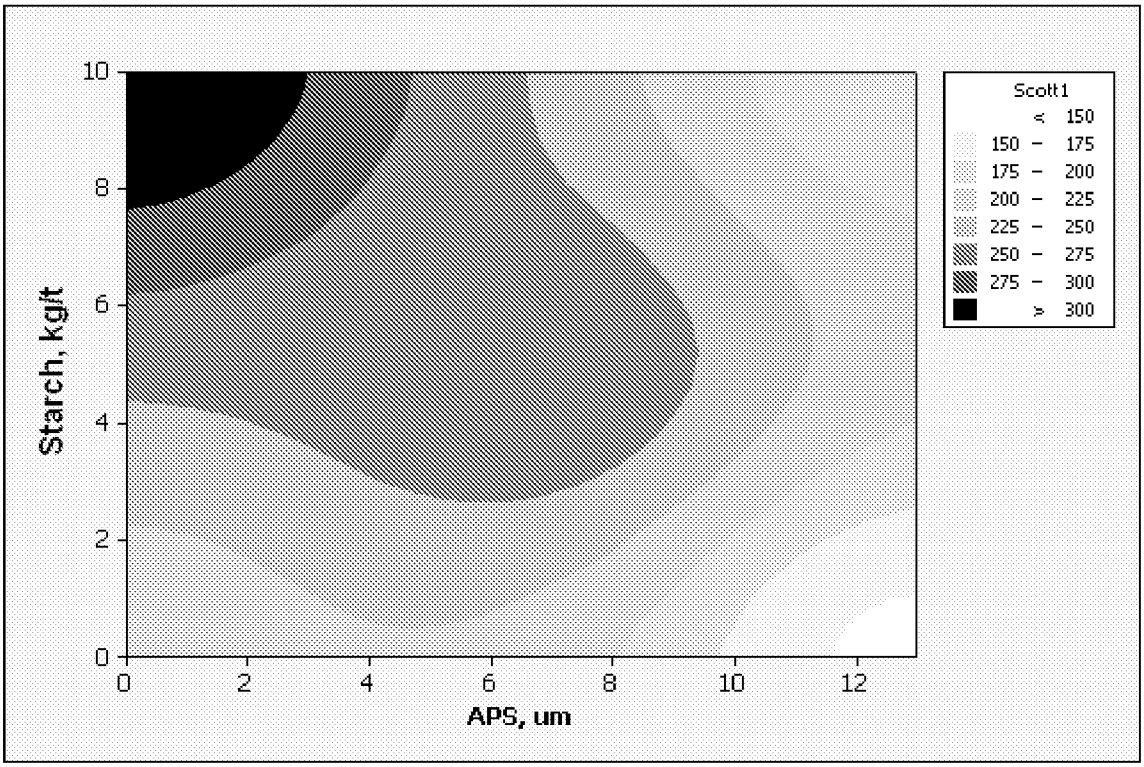

Scott1
≤ 150
150 – 175
175 – 200
200 – 225
225 – 250
250 – 275
275 – 300
> 300
Starch, kg/t
APS, um
0
2
4
6
8
10
12

Fig. 3

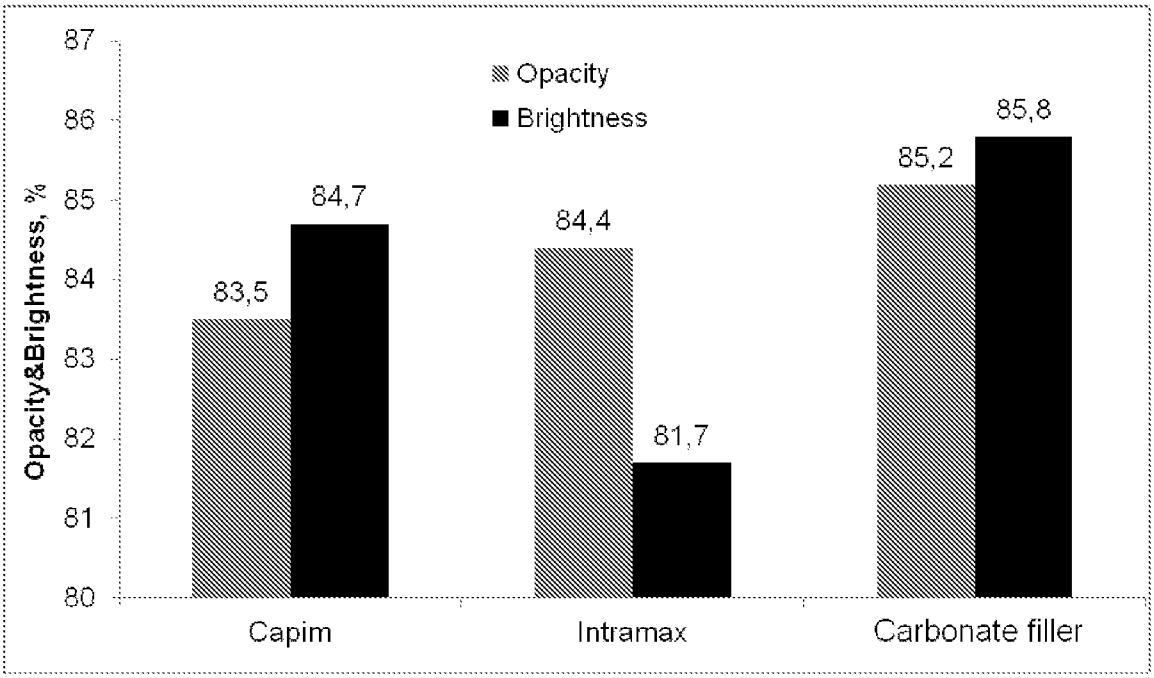
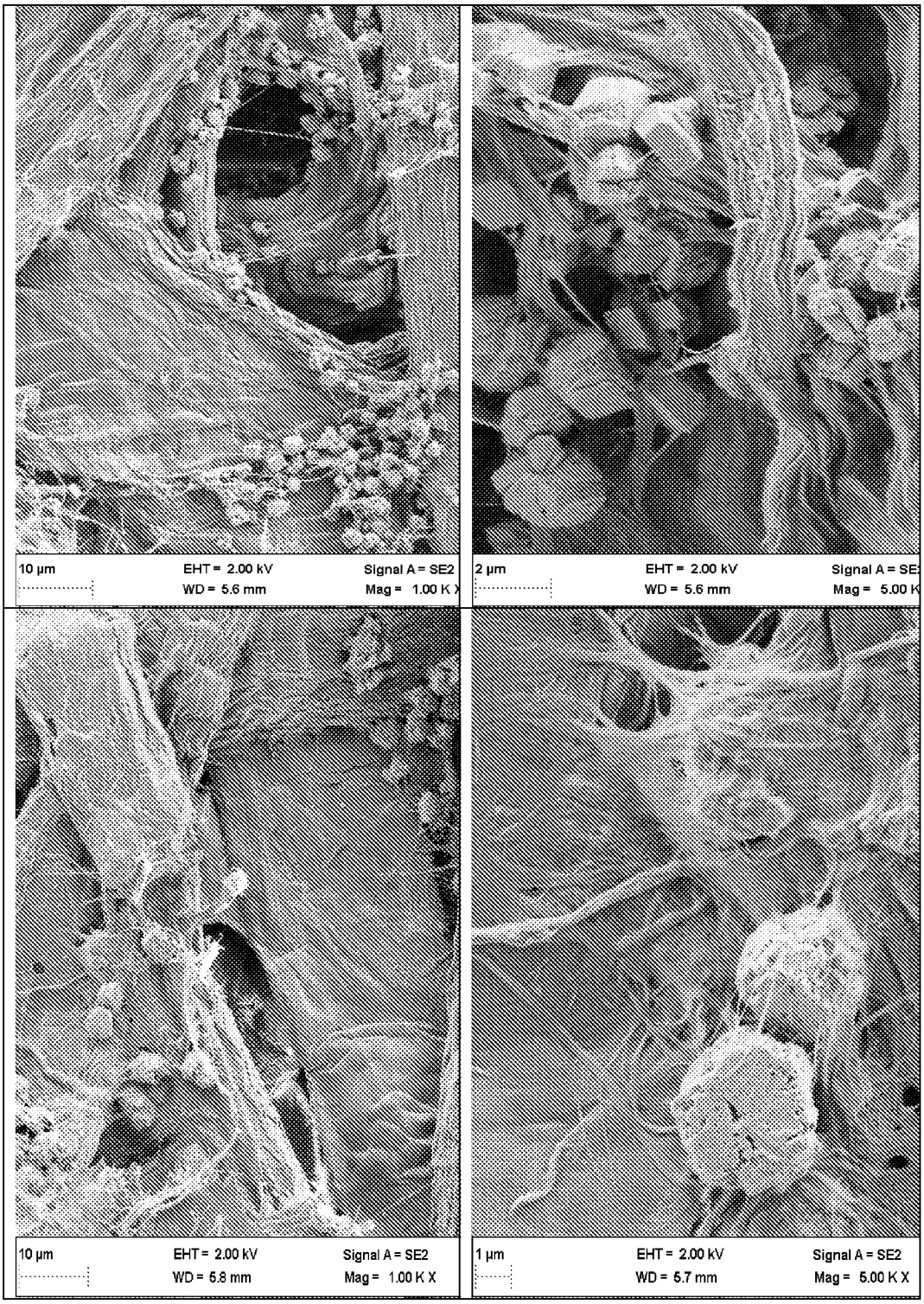

Opacity
Brightness
Opacity&Brightness, %
87
86
85
84
83
82
81
80
83,5
84,7
84,4
81,7
85,2
85,8
Capim
Intramax
Carbonate filler

Fig. 4


10 µm
EHT = 2.00 kV
WD = 5.6 mm
Signal A = SE2
Mag = 1.00 K X
2 µm
EHT = 2.00 kV
WD = 5.6 mm
Signal A = SE
Mag = 5.00 K
10 µm
EHT = 2.00 kV
WD = 5.8 mm
Signal A = SE2
Mag = 1.00 K X
1 µm
EHT = 2.00 kV
WD = 5.7 mm
Signal A = SE2
Mag = 5.00 K X

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2012/051286

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09C1/02
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 387 212 B1 (CHRISTIAN RICHARD [FR]) 14 May 2002 (2002-05-14)	9-13,18
A	claims 1-20 column 6, line 23 - column 7, line 55	1-8, 14-17

X	WO 2007/057509 A1 (NORDKALK OYJ ABP [FI]; VIRTANEN PENTTI [FI]) 24 May 2007 (2007-05-24)	9-13,18
A	claims 1-23 page 14, line 6 - page 18, line 17	1-8, 14-17

X	WO 2011/151525 A1 (NORDKALK OY AB [FI]; VIRTANEN PENTTI [FI]; SAASTAMOINEN SAKARI) 8 December 2011 (2011-12-08)	9-13,18
A	claims 1-23 page 14, line 13 - page 25, line 28	1-8, 14-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Gerwann, Jochen

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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		WO 2011151525 A1	08-12-2011

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权利要求书2页 说明书11页 附图3页

(54)发明名称

纤维产品的制造中沉淀碳酸盐的使用

(57)摘要

本发明涉及一种填料或填料混合物，其含有碳酸盐，以及涉及一种用于通过将填料直接沉淀到纸浆中制造其的方法，或一种不存在特别是来自纸张或纸板制造业的白水的纤维的单独方法。本发明还涉及含有此填料的纤维产品，例如纸张纸板产品，或塑料、橡胶、混凝土或油漆产品。

CN 104204107 A

1. 一种用于制造含有碳酸盐的填料的方法，其特征在于

通过向溶液添加二氧化碳由对应的氢氧化物溶液形成酸性碳酸氢盐离子溶液，和

通过借助于负压或离心力或它们的组合将所得酸性碳酸氢盐离子溶液的 pH 增加至中性或碱性范围，形成所述填料的碳酸盐部分。

2. 根据权利要求 1 所述的方法，其中氢氧化钙或氢氧化镁或它们的混合物用作氢氧化物。

3. 根据权利要求 2 所述的方法，其中通过在水中淘析煅石灰、煅烧白云石、MgO、或钙、钠或镁的其它此类来源或通过淘析上述两种或更多种物质的混合物，制造氢氧化钙、氢氧化钠、或氢氧化镁，在水中淘析时所述来源提供碱性溶液。

4. 根据前述任一项权利要求所述的方法，其中所述氢氧化物和所述二氧化碳大致同时加入。

5. 根据权利要求 1 至 3 中任一项所述的方法，其中二氧化碳在单独阶段中加入所述成品氢氧化物溶液。

6. 根据前述任一项权利要求所述的方法，其中将额外富矿物填料如 GCC、PCC、硅灰石、高岭土、滑石粉、白垩、缎光白、或它们的混合物加入所述酸性碳酸氢盐离子溶液，之后由所述溶液形成所述填料的碳酸盐部分。

7. 根据前述任一项权利要求所述的方法，其中通过浸润、沉积、挤压、蒸发、干燥、或借助于离心力增加所得碳酸盐填料的干物质。

8. 根据前述任一项权利要求所述的方法，其中所述氢氧化物溶液选自这种水溶液或水性纸浆，其属于含有化学纸浆纤维、木材纤维、或合成纤维或它们的混合物的纤维产品的所述制造方法的聚集体或加工用水。

9. 一种填料或填料混合物，其含有碳酸盐，其特征在于至少其碳酸盐部分是通过根据权利要求 1 至 8 中任一项所述的方法来制造。

10. 根据权利要求 9 所述的填料，其含有碳酸钙、碳酸钠或碳酸镁、或它们的混合物，并且优选地由碳酸钙、碳酸钠、或碳酸镁或它们的混合物组成。

11. 根据权利要求 9 或 10 所述的填料，其含有研磨碳酸钙 (GCC)、沉淀碳酸钙 (PCC) 或它们的混合物和任选的硅灰石作为所述碳酸盐部分。

12. 根据权利要求 9 至 11 中任一项所述的填料，其被混合至干强度聚合物，所述干强度聚合物优选选自淀粉、醛淀粉、瓜耳胶、聚丙烯酰胺、乙醛酸化聚丙烯酰胺、羧基甲基纤维素、聚乙烯醇、胶乳或壳聚糖、或上述两个或更多个的混合物，最合适地是选自淀粉。

13. 根据权利要求 9 至 12 中任一项所述的填料，其处于中性或碱性 pH。

14. 一种用于制造含有化学纸浆纤维、木材纤维或合成纤维、或它们混合物的纤维产品的方法，其中制造纤维纸浆，其中使用含碳酸盐填料，其后所述纤维产品由所述纸浆压缩并且任选地涂布，其特征在于在所述纸浆压缩成所述纤维产品之前，所述所用填料的至少所述碳酸盐部分在用于制造所述纸浆的水溶液中形成，或其在所述纤维产品的所述任选涂布之前，通过使用根据权利要求 1 至 8 中任一项所述的方法在涂层混合物中形成。

15. 根据权利要求 14 所述的方法，其中 GCC 或 PCC 或它们的混合物用作所述填料的碳酸盐部分或其一部分，并且其中所述填料还可含有硅灰石。

16. 根据权利要求 14 或 15 所述的方法，其中在所述纤维产品的制造中所用的机器的前

箱之前，将所述填料的至少碳酸盐部分形成为水溶液。

17. 根据权利要求 14 至 16 中任一项所述的方法，其中制造纸张或纸板产品。

18. 根据权利要求 9 至 13 中任一项所述的填料在塑料、混凝土、橡胶、或油漆中的用途。

纤维产品的制造中沉淀碳酸盐的使用

技术领域

[0001] 本发明涉及一种填料或填料混合物，其含有碳酸盐，并涉及一种用于通过将填料直接沉淀到纸浆中制造其的方法，或一种不存在特别是来自纸张或纸板制造业的白水的纤维的单独方法。本发明还涉及含有所述填料的纤维产品，例如纸张纸板产品，或塑料、橡胶、混凝土或油漆产品。

[0002] 现有技术描述

过去几十年内，对沉淀碳酸钙的需求一直已迅猛增长，尤其是在纸张和纸板制造，橡胶和塑料的加工和印刷油墨、油漆和粘合剂的制造中。沉淀碳酸钙具有优良亮度和散射能力，以及低价格。此外，当用于上述应用中时，沉淀碳酸钙可以增加机械强度。

[0003] 这些碳酸钙具有通常呈方解石、霰石或球霰石形式的晶体结构。方解石通常发现呈晶体形式，例如偏三角面体、菱形、立方体、和棱柱形式。霰石为斜方晶，并且其通常发现呈细长形式。在正常温度和压力下，球霰石为不稳定，易变为方解石和霰石。一般来说，球霰石具有球形形状。通过改变反应条件例如熟石灰的浓度和反应温度，晶体形式可以转变为针状、立方体、球形和许多其他晶体形式。

[0004] 由于氢键，主要在纤维与细粒的带电基团之间发展出纸张和纸板的强度。这些带电基团特别包括羟基和羧基。当改善强度时，主要通过研磨纤维以机械方式来改善，从而尝试增加纤维的纤化。该强度取决于个体纤维等级的强度，纤维之间的强度，纤维键的数量，以及成品纸张或纸板中纤维和键的分布。

[0005] 通常，纸张和纸板的制造中所用的填料或颜料具有小于 5 μm 的平均粒度，并且它们具有浅色。最典型的填料包括高岭土、滑石粉、研磨碳酸钙 (GCC) 和沉淀碳酸钙 (PCC)。另外，存在更昂贵的特殊颜料，例如沉淀硅酸铝、缎光白和二氧化钛。填料和涂层颜料之间划分确切界限很困难，但大体上填料具有比涂层所用颜料更大的粒度和更粗糙的形状。理论上，从最大光散射的角度来看，最常用填料和涂层颜料的最佳粒度为约 0.4 至 0.5 μm。然而，通常来说，涂层颜料的平均粒度为 0.5 至 1 μm，并且填料的平均粒度为 1.5 至 4 μm。

[0006] 使用填料和颜料以及其他填料的最大缺点是当特别是用填料置换化学物质时削弱纸张或纸板结构的强度。这是由使填料附接至纤维的表面而阻止纤维之间氢键的生成所导致。然而，研磨形式 (GCC) 和沉淀形式 (PCC) 的碳酸钙广泛使用，因为特别是在化学纸浆的纤维的置换中，它们价格低且光散射性质良好。由再循环、去油墨和机械纸浆制造的纸张和纸板可能由碳酸钙置换，但碱导致的机械木浆颜色变深常常限制其在由这些纸浆制造的纸张和纸板等级的制造中的使用。

[0007] 历史上，已特别通过将单个填料粒子附聚成较大附聚体减少了添加填料所致的强度降低问题。除了别的以外，这已示于 US 专利说明书 4 225 383、4 115 187、4 445 970、5 514 212 和 4 710 270 中以及 GB 公布 2 016 498 和 1 505 641 中。通常，这些中的阴离子填料粒子已用混合物中的阳离子添加剂附聚成较大聚集体。已观察到以此方式已改善了强度特性和填料保持，但同时光学性质下降。

[0008] 还有一些公布，其中使用胶乳来减小填料添加所致的强度降低。除了别的以外，这

示于 US 专利说明书 4 178 205、4 189 345、4 187 142、4 710 270 和 7 074 845 中。

[0009] 当纤维被填料置换时纸张或纸板产品的强度和刚度的降低主要由填料削弱纤维之间氢键的生成所导致，因为填料的表面不形成氢键。目前，该填料一般被直接加入纸浆。在金属丝(wire)段中，仅一部分的添加填料附接到成品纸张或纸板卷材。无论如何，其余部分的填料通过白水系统引导以形成成品纸张或纸板结构的一部分，但主要由于各种疏水性物质附接至白水系统的填料，各种运行性问题的风险已增加。一般来说，纸张或纸板机器中的这些运行性问题例作为金属丝和毡圈的污染以及最终作为断裂物出现。白水系统的填料的一部分还最终增加污水处理厂负担，因为不是所有材料都随成品纸张或纸板一起被携带出该工艺。填料导致的纸张或纸板的表面上的较弱纤维－纤维键还可能导致印刷期间表面的粉尘形成增加。

[0010] 因此，需要一种纤维产品，其中填料将附接至纤维并且其他填料更有效地并同时地将提供具有与已知解决方案相比进一步提高的有利强度性质的产品。

[0011] 本发明的简要说明

本发明的一个目的为提供一种新纤维产品，例如纸张或纸板产品，其具有高强度、亮度、油墨密度和不透明度。

[0012] 具体来说，本发明的一个目的为提供一种新含碳酸盐填料，其可用于这种纤维产品中，尤其是使得碳酸盐填料附着至纤维产品的纤维之间的间隙。

[0013] 例如，可以通过根据本发明的方法提供这种含碳酸盐填料和纤维产品。

[0014] 本发明因此涉及含碳酸盐的填料和其生产方法。这种填料还用于制造根据本发明的纤维产品的方法中，其中所述纤维产品含有化学纸浆纤维和 / 或木材纤维和 / 或合成纤维，并且其优选为纸张或纸板。在制造纤维产品的这种方法中，碳酸盐填料附着在化学纸浆纤维或木材纤维之间并且附着至小纤维，此后由该纸浆生产所述纤维产品。

[0015] 更精确地，制造根据本发明的含碳酸盐填料的方法的特征在于权利要求 1 的特征部分所述内容。

[0016] 根据本发明的含碳酸盐填料或填料混合物的特征又在于权利要求 9 的特征部分所述内容。

[0017] 相应地，制造根据本发明的纤维产品的方法的特征在于权利要求 14 的特征部分所述内容，并且根据本发明的填料的用途的特征在于权利要求 18 所述内容。

[0018] 使用本发明达到若干显著优点。已证明，通过在形成含碳酸盐填料时使用低压，实现使用碳酸盐的最终产品如纸张或纸板的亮度、强度、不透明度和可印刷性（油墨的吸收性）的改进。因此，最终产品的纤维的一部分可由填料置换，使得与使用常规填料时相比，强度性质同时维持在较佳水平。

[0019] 当增加干强度的聚合物在填料中与碳酸盐一起使用时或在纤维产品的制造中与该填料一起使用时，实现特别有利的性质。

[0020] 为增加 pH 并在负压中形成碳酸盐，在不添加单独化学物质(即，碱)的情况下从反应混合物中释放二氧化碳是足够的。这对纸张和纸板厂是特别的优点，在纸张和纸板厂中存在可从纸浆厂获得的游离二氧化碳的能力。

附图说明

[0021] 图 1 是当在纤维网络中使用 80 g/m² 的基重和 10% 的碳酸盐填料时，碳酸盐填料 (APS) 的粒度和一部分淀粉对纤维产品的 TEA 值 (TEA1) 影响的图形描述。

[0022] 图 2 是当在纤维网络中使用 80 g/m² 的基重和 10% 的碳酸盐填料时，碳酸盐填料 (APS) 的粒度和一部分淀粉对纤维产品的史考特粘结值 (Scott1) 影响的图形描述。

[0023] 图 3 是高岭土和碳酸盐填料 (粒度级别 6.5 μm) 的亮度值和不透明度值的图形描述。结果以 80 g/m² 基重归一化为 6% 的填料含量。

[0024] 图 4 示出 80 g/m² 的化学纸浆薄板的扫描电子显微镜图像，其包含薄板的表面上 13 μm (上行) 和 6.5 μm (下行) 的粒度级别的碳酸盐填料。

[0025] 本发明的优选实施方案的详细描述

在碳酸盐的常用沉淀方法中，通过将 pH 从碱性朝中性改变，制造沉淀碳酸钙 (PCC)。在根据本发明的碳酸盐填料的制造中，pH 从酸性增加至高于 7 的 pH。目的是在沉淀阶段提供碳酸盐，其与增加干强度的可能聚合物一起可提高最终产品中含填料网络的强度，而不削弱光学性质 (不透明度和亮度)。

[0026] 本发明因此涉及一种制造含有碳酸盐的填料的方法，其中酸性碳酸氢盐离子溶液通过将二氧化碳加入所述氢氧化物溶液由相应的氢氧化物溶液形成，此后通过借助于减压或离心力或它们的组合将形成的酸性碳酸氢盐离子溶液的 pH 增加到中性或碱性范围形成填料的碳酸盐部分。

[0027] 在上下文中“酸性”是指低于 7 的 pH 值，而“中性”是指 7 至 8 的 pH 值，并且“碱性”是指高于 8、特别是高于 10 的 pH 值。

[0028] 在上下文中“减压或负压”是指环境压力或空气压力以下的压力，优选在 0.60 至 1 巴的范围内，即绝对压力 0.4 至 0 巴；更优选在 0.85 至 0.95 巴的范围内，即绝对压力 0.15 至 0.05 巴；特别是在 0.88 至 0.94 巴的范围内，即绝对压力 0.12 至 0.06 巴。

[0029] 当利用离心力时，优选使用 50 至 2000 rpm (转每分钟) 的旋转速度。

[0030] 进行该方法的所述阶段时的温度可接近于环境温度 (约 25℃) 或稍高、特别是 35 至 70℃。

[0031] 所用氢氧化物优选为氢氧化钙或氢氧化镁或它们的混合物。更优选地，通过在水或水溶液中淘析煅石灰、煅烧白云石、MgO 或钙或镁的其它来源或通过淘析上述两种或更多种物质的混合物，制造所用氢氧化物，所述来源在这样的溶液中淘析时提供碱性溶液。

[0032] 氢氧化物和二氧化碳可以基本上同时加入所述水溶液。任选地，它们在不同阶段加入。

[0033] “水溶液“是指含有大于 50 重量 % 水的所有溶液或悬浮液。因此，水溶液包括纯水 (100 重量 % 水) 和稀释纤维悬浮液。

[0034] 纸张或纸板机的任何水溶液可转变成适用作本方法的起始物质溶液的碳酸氢盐离子溶液。优选地，所述水溶液为纸张或纸板制造的工艺用水，特别是循环水。

[0035] “碳酸氢盐离子溶液”为含有碳酸根的各种状态的水溶液，其 pH 处于其中碳酸根的状态大概主要呈碳酸氢根形式的范围内；就这一点而言，特别是在 4 至 10 的 pH 范围内。

[0036] 当改变例如根据本发明的含有碳酸根 - 或碳酸氢根的溶液的 pH 时，其碳酸根状态也根据所谓碳酸根体系而变化。碳酸根的主要状态为：

$$H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$$

在酸性 pH 下，可溶二氧化碳 (CO_2) 和（较小程度上）碳酸 (H_2CO_3) 是碳酸根的主要状态。在中性 (pH 7 两侧）和碱性范围中，碳酸氢根（bicarbonate）或碳酸氢根 (hydrogen carbonate) (HCO_3^-) 为 pH 高达约 10 的碳酸根的主要状态。在高碱性范围 (pH > 10) 中，碳酸根 (CO_3^{2-}) 为主要状态。

[0037] 碳酸根的碱度是指用强酸可将水溶液滴定至酚酞终点的强酸含量。在此点，所有 CO_3^{2-} 已被转变成离子状态 HCO_3^-。这在 pH 约 8.3 处发生。在纸张和纸板制造的最重要 pH 范围（pH 6－8）中，碳酸氢根 (HCO_3^-) 为主导状态。此外，相当良好溶解的二氧化碳和一些碳酸和胶态碳酸根已从该 pH 范围的酸性侧进入此 pH 范围内。

[0038] 酸性 pH 范围 (pH < 6) 内的溶液此处称为酸性碳酸氢根离子溶液。

[0039] 在本发明中，碳酸根由溶液中的碳酸氢根离子形成。通过增加 pH 或温度可以使碳酸氢根离子从碳酸根离子溶液中沉淀为碳酸盐粒子是常识。

[0040] 当温度增加时，释放二氧化碳并且碳酸氢根与例如游离钙或镁离子根据以下反应公式反应：

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O \uparrow 。$$

[0041] 相应地，当用碱如 NaOH 或 $Ca(OH)_2$ 增加 pH 时，碳酸盐粒子可以根据以下反应公式沉淀：

$$Ca^{2+} + 2HCO_3^- + 2NaOH \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O。$$

[0042] $$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2OH^-。$$

[0043] 然而，本发明是基于这样一种情况，其中足够温热（至少室温）的碳酸氢根离子溶液经受减压或受离心力作用，使得二氧化碳从溶液中释放到空气。

[0044] 特别地，已证明，在碳酸盐填料的这种制造中例如直接在纸张或纸板厂的加工中，通过使用减压，实现最终产品如纸张或纸板的强度、不透明度和可印刷性（油墨的吸收性）的改善。当增加干强度的聚合物与填料中的碳酸盐一起使用时，或用于用该填料制造的最终产品中时，这些优点进一步增强。

[0045] 为在减压下增加 pH 并形成碳酸盐，在无单独化学物质如碱的情况下从处于酸性 pH 下的上述碳酸氢根离子溶液中释放二氧化碳是足够的。这对纸张和纸板厂是特别的优点，在纸张和纸板厂中存在可从制造酸性碳酸氢根离子溶液的纸浆厂获得的游离二氧化碳的能力。

[0046] 在纸张和纸板工业中，碳酸钙常用作碳酸盐，既用作填料也用作涂层颜料。碳酸钙的熟知形式包括研磨碳酸钙 (GCC) 和沉淀碳酸钙 (PCC)。常规地，目标是保持它们的平均粒度大于 500 nm，通常 1 至 2 μm，据信因此实现最佳可能光散射效率（亮度和不透明度）。在正常条件下它们的水中溶解度相当低。然而，在酸性条件下释放可溶性钙离子，增加水的硬度。

[0047] 根据本发明制造的碳酸盐的平均粒度 (APS50) 优选为 0.5 至 15 μm、特别是 1 至 8 μm。

[0048] 在由该溶液形成填料的碳酸盐部分之前，可将其他填料加入本发明中所用的酸性碳酸氢根离子溶液。这种添加填料优选为商用 GCC 或 PCC 或它们的混合物，或任选地是碳酸盐之外的填料，例如硅灰石、硅酸铝、高岭土、滑石粉、缎光白或二氧化钛。

[0049] 在上下文中“碳酸盐部分”是指将形成或在线形成的填料或填料混合物的固体碳

酸盐，从而描述与所添加填料或相应添加剂相比的碳酸盐含量。该部分优选 > 5%。

[0050] 还有可能增加含有碳酸盐的所得填料溶液的干物质含量。这具体来说通过浸润、沉积、挤压、蒸发、干燥、或借助于离心力来进行。

[0051] 根据本发明的实施方案，干强度聚合物与填料的碳酸盐部分一起使用，优选选自淀粉、醛淀粉、瓜耳胶、聚丙烯酰胺、乙醛酸化聚丙烯酰胺、羧基甲基纤维素、聚乙烯醇、胶乳或壳聚糖、或上述两种或更多种的混合物，最优选选自淀粉。

[0052] 在纸张或纸板工业，使用填料所致的干强度降低通常已使用水溶性天然和人工聚合物来补偿。填料的使用增加使用干强度剂的需要。最典型的干强度剂包括淀粉、羧基甲基纤维素 (CMC)、瓜耳胶和聚丙烯酰胺 (PAM)。聚乙烯醇和胶乳也可以用作干强度聚合物，即便在实践中，它们也一般不用于纸张或纸板制造方法的湿润段。

[0053] 在增加纤维网络的强度中，淀粉是最老和最常用干强度剂，其强度增加影响是通过其增加氢键生成的大量羟基所致。阳离子性和两性淀粉是最常用淀粉。一般来说，当这些被加入高稠度纸浆时，效果主要为强度性质增加。除了阳离子化之外，在羧基甲基纤维素 (CMC) 的制造中，可以在淀粉中形成醚键。天然淀粉可以被进一步酯化、氧化、水解并且使用酶和加热的组合或上述中的一些或全部来处理。天然淀粉的最典型来源为马铃薯、大麦、小麦、玉米和木薯。然而，当被加入稀释纸浆或短循环纸浆时，淀粉改善细粒和填料的保持，而非增加强度。

[0054] 另外，淀粉以库存尺寸如 AKD 和 ASA 的分散体使用。纸张的表面上胶以及纸板的各种层彼此附着常常用淀粉进行。

[0055] 根据特别优选的实施方案，制造碳酸盐填料，首先通过同时或在煅石灰或白云石或它们的相应氢氧化物溶液被加入水溶液之前，向水溶液定量加入二氧化碳，使水溶液变酸性。然后获得根据本发明的碳酸氢盐离子溶液，其已酸化。随后，通过减压使溶液的 pH 增加至中性或碱性范围，从而生成根据本发明的碳酸盐填料。

[0056] 本发明还涉及含有借助于上述方法制造的碳酸盐的填料或填料混合物。因此，通过一种方法制造所考虑的填料或填料混合物，其中借助于减压或离心力或它们的组合使 pH 从酸性范围增加至中性或碱性区域。

[0057] 该填料含有至少 5 重量 %、优选 25 至 100 重量 %、最合适是 50 至 90 重量 % 的碳酸盐，所述碳酸盐已在水溶液中以固体形式形成。该碳酸盐的平均粒度优选为 0.5 至 15 μm、特别是 1 至 8 μm。该碳酸盐优选选自碳酸钙或碳酸镁或它们的混合物。最合适地，该填料由碳酸钙或碳酸镁或它们的混合物组成。就本发明而言特别优选的填料是研磨碳酸钙 (GCC)、沉淀碳酸钙 (PCC) 或它们的混合物。

[0058] 根据本发明形成的填料的 pH 为中性或碱性。填料的最终 pH 值优选为 6 至 8。

[0059] 根据本发明在线制造的碳酸盐也可以与另外的填料混合成填料混合物。这种添加填料优选为商用 GCC 或 PCC 或它们的混合物，或任选地，其含有碳酸盐之外的填料，例如硅灰石、硅酸铝、高岭土、滑石粉、缎光白或二氧化钛。

[0060] 根据本发明的实施方案，填料的碳酸盐部分在已与干强度聚合物混合的最终填料中，最优选在纸浆中，所述聚合物优选选自淀粉、醛淀粉、瓜耳胶、聚丙烯酰胺、乙醛酸化聚丙烯酰胺、羧基甲基纤维素、聚乙烯醇、胶乳或壳聚糖、或上述两种或多种的混合物，最优选选自淀粉。

[0061] 本发明还涉及一种制造含有化学纸浆纤维、木材纤维或合成纤维、或它们的混合物的纤维产品的方法。在此方法中，制造该纸浆，向其添加含碳酸盐填料，然后将该纸浆压缩成纤维产品，该纤维产品任选被涂布。

[0062] 所用填料或填料混合物，任选地与水溶性的、干强度增加聚合物一起，增加待制造纤维产品的结构的光学性质，并且保持其强度性质。

[0063] 纤维产品是指薄、片状纤维产品，其特别是纸张或纸板产品。

[0064] 该产品的纤维可以是任何天然纤维或合成纤维或它们的混合物。特别地，纤维可以是化学纸浆或机械纸浆或它们的混合物。例如，硫酸盐和亚硫酸盐纤维素纤维，溶解纸浆，纳米纤维素，化学机械的 (CTMP)、热机械压力碎木 (TMP)，压力碎木 (PGW)，碎木纸浆，再循环纤维，或去油墨纸浆的纤维可以构成该产品的纤维。通常，硫酸盐和亚硫酸盐纤维素称为化学纸浆，并且热机械纸浆、压力碎木和碎木纸浆称为机械纸浆。当向其添加根据本发明的填料或填料混合物时，由这些纤维制成的纸浆的密度优选为 0.1 至 5%、特别是 0.2 至 1.5%。

[0065] 在纸张或纸板制造方法中，“填料”特定指所述粒子，其被添加或附着至纤维之间的间隙，并且其目的是降低最终产品的纤维含量。就本发明而言，该定义也涵盖颜料，包括涂层颜料。

[0066] 通常，纸张和纸板制造的这种已知填料和颜料具有小于 5 μm 的平均粒度，并且它们具有浅色。最典型的填料包括高岭土、滑石粉、研磨碳酸钙 (GCC) 和沉淀碳酸钙 (PCC)。另外，存在更昂贵的特殊颜料，例如沉淀硅酸铝、缎光白和二氧化钛。填料和涂层颜料之间划分确切界限很困难，但大体上填料具有比涂层所用颜料更大的粒度和更粗糙的形状。理论上，从最大光散射的角度来看，最常用填料和涂层颜料的最佳粒度为约 0.4 至 0.5 μm。然而，通常来说，涂层颜料的平均粒度为 0.5 至 1 μm，并且填料的平均粒度为 1.5 至 4 μm。

[0067] 根据本发明，在纸浆压缩成纤维产品之前，纤维产品中所用填料的至少碳酸盐部分在待用于纸浆的制造的水溶液中形成，或其在纤维产品的任选涂布之前形成在涂布糊剂中。因此，当纤维产品为纸张或纸板产品时，那么其中形成碳酸盐部分的水溶液是纸张或纸板制造的工艺用水，优选是循环水，特别是在机器前箱之前的循环水。

[0068] 为制备填料的碳酸盐，使用上述方法，其中借助于减压或离心力或它们的组合，pH 从酸性范围增加至中性或碱性范围。

[0069] 待形成的碳酸盐优选为碳酸钙或碳酸镁或它们的混合物。

[0070] 在将其加入纤维之前，也可能增加含有碳酸盐的填料溶液的干物质含量。具体来说，这通过浸润、沉积、挤压、蒸发、干燥、或借助于离心力来进行。

[0071] 根据本发明的实施方案，干强度聚合物与填料的碳酸盐部分一起在纸浆中使用，优选选自淀粉、醛淀粉、瓜耳胶、聚丙烯酰胺、乙醛酸化聚丙烯酰胺、羧基甲基纤维素、聚乙烯醇、胶乳或壳聚糖、或上述两种或多种的混合物，最合适选自淀粉。

[0072] 在本发明中，任选使用的淀粉量为纸浆的 0 至 40 kg/t。从该极限处增加添加削弱金属丝部分(wire section)的脱水等。这是由纤维的阴离子电荷和填料被阳离子淀粉中性化所导致，因此淀粉的其余部分不再附着至纤维和填料，但以溶解淀粉形式保持在循环水中。

[0073] 以下非限制性实例说明本发明和其优点。

实施例

[0074] 以下实例说明造纸技术的若干性质的改进，这借助于根据本发明的碳酸盐填料实现。

[0075] 理论上，可能认为，当比纤维更亮的碳酸盐填料并入到纤维网络时，根据本发明制造的纤维产品的结构能改善产品的不透明度和可印刷性。这改善光散射和油墨的吸收。

[0076] 相同填料和填料含量下强度性质的增加是由于当与纤维汇集时碳酸盐填料仍为不稳定的无定形状态，从而碳酸盐填料能够增加干强度聚合物的羟基和纤维的氢键基团之间的强度键。

[0077] 实施例 1（酸性碳酸氢盐溶液的制造）

通过在 45℃下将 100 或 200 g 煅石灰 (CaO) 分别与 500 g 或 1000 g 水混合，制造酸性碳酸氢盐离子溶液。将如此生成的 $Ca(OH)_2$ 浆液加入 30 升自来水中。随后，使水和氢氧化钙与输送到该混合物的二氧化碳反应，使得反应结束时混合物的 pH 为 6.3。沉积 12 小时之后，沉积在底部上的沉淀与溶解和胶态的材料 (Ca 离子、碳酸、碳酸氢盐和胶态碳酸钙）分离。沉积在底部上的沉淀物不用于该测试。如此制造的碳酸氢盐离子溶液用作下述沉淀测试中的原材料。

[0078] 进一步使用如此制造的酸性碳酸氢盐离子溶液的一部分，使得将其整个固体物质（以及沉积部分）加热到 50℃并减压 5 分钟至 0.92 巴，即 0.08 巴的绝对压力。在 50 升钢容器中进行减压。借助于泵产生减压。因此，获得表 1 的粒度 (APS10、APS50 和 APS90)、传导率和 pH。

[0079] 表 1. 每 30 升水 100 和 200 g CaO。将所有固体物质减压。

gCaO/30L	APS10, μm	APS50, μm	APS90, μm	传导率, μS/cm	pH
100	2.8	8.5	28.5	460	7.5
200	1.3	6.2	13.8	450	7.5

[0080] 在上表 1 中，减压之后，30 升的 100 g CaO 含有 5.6 g/l 碳酸盐。减压之后，30 升的 200 g CaO 含有 11.3 g/l 碳酸盐。

[0081] 实施例 2（作为单独方法的碳酸氢盐的沉淀）

在此实例中，使用根据先前实施例制造的碳酸氢盐离子溶液 (30 升)，已将 100 g 氧化钙加入其中之一并且将 200 g 氧化钙加入另一份。沉积在底部上的沉淀物不用于该测试。将碳酸氢盐溶液加热到 55℃，然后在 50 升钢容器中允许 0.92 巴（即，0.08 巴的绝对压力）的减压以影响碳酸氢盐离子溶液。借助于泵产生减压。

[0082] 表 2 和 3 示出样品取出减压容器前的滞后时间和样品的测量性质。

[0083] 表 2. 每 30 升水 100 g 氧化钙 (CaO)。

时间, 秒	APS10, μm	APS50, μm	APS90, μm	传导率, (μS/cm	pH
0	1.1	8.3	31.0	1430	6.63
30	3.3	5.7	10.5	970	7.29
120	4.3	8.8	22.3	830	7.31
240	4.2	9.4	23.0	676	7.40
600	3.7	7.6	16.4	550	7.40

[0084] 表 3. 30 升水 200 g 氧化钙 (CaO)。

时间, 秒	APS10, μm	APS50, μm	APS90, μm	传导率, μS/cm	pH
0	2.3	11.0	28.2	1115	6.55

30	0.8	7.2	18.3	790	7.26
120	1.0	7.6	18.2	740	7.27
240	1.0	6.7	16.3	740	7.34
600	3.3	13.2	26.0	690	7.43

[0085] 上表 2 和 3 示出减压 30 秒的 100 g CaO/30 l 产生最小的平均粒度 (APS50)。减压 600 秒的 200 g CaO/30 l 提供平均粒度 (APS50) 最大的碳酸盐粒子。用 Malvern Mastersizer 2000 测量粒度 (APS10、APS50 和 APS90)。两个表均表明伴随二氧化碳从碳酸氢盐溶液释放，酸性溶液变得中性和碱性。虽然减压下 pH 增加，但当钙离子从碳酸根离子沉淀碳酸盐粒子时传导率降低。

[0086] 实施例 3（用存在的纤维沉淀碳酸氢盐）

在实验室测试中，使用研磨成 SR 数 30 的松树纸浆和桦树纸浆。所述纸浆中，70% 为松树纸浆并且 30% 为桦树纸浆。纸浆的密度为 3.8%。从该纸浆中，通过约 0.2% 密度下的薄板模具制得 80 g/m^2 的薄板。对照样品用自来水稀释至 0.2% 的密度。在测试点将所述碳酸氢盐离子溶液（表 3）稀释至 0.2% 密度，在所述溶液中的一些内形成 6.5 μm 或 13 μm 的碳酸盐填料。在以下结果中，如果未单独另外说明，填料含量归一化至 6% 的水平。对照测试点为：

Capim SBF, Imerys（和 10 kg/t 淀粉，添加到 3.8% 纸浆），下文称 Capim

Intramax, Imerys（和 10 kg/t 淀粉，添加到 3.8% 纸浆），下文称 Intramax

对照 1，即由无淀粉的化学纸浆纤维制成的薄板

对照 2，即 5 kg/t 淀粉，添加到 3.8% 纸浆

对照 3，即 10 kg/t 淀粉，添加到 3.8% 纸浆

由如此制造的 0.2% 稠度的纸浆，根据标准 SCAN-C 26:76 (SCAN-M 5:76)，不用循环水，在薄板模具中生产 80 g/m^2 的薄板（来自各测试点的 10 个薄板）。此后，薄板在鼓式干燥器中 105℃下干燥两个小时，然后将它们取出在 23℃和相对湿度 50% 下吹风 48 小时。此后，核实它们的基重并且测定以下性质：

- 填料含量 (525℃，2 小时）
- ISO 亮度 (L&W Elrepho 分光光度计 SE070), ISO 2470
- 不透明度 (L&W Elrepho 分光光度计 SE070), ISO 2471
- 史考特粘结值（内部粘结测试仪 Huygen)，TAPPI-UM403
- TEA (L&W 张力和断裂韧度测试器)，SCAN-P 38:80

在减压下制造的碳酸盐填料的粒度和纸浆淀粉的部分之间，进行根据测试计划的析因试验，变量如下：

- 纸浆淀粉 0、5 和 10 kg/t 的部分
- 碳酸盐填料 0、6.5 和 13 μm 的平均粒度 (APS)。

[0087] 对于测试的中点，即 5 kg/t 淀粉和 6.5 微米碳酸盐填料的粒度 (APS)，进行两次重复以明确统计可靠性。根据先前实施例 2 选择用于粒度的减压条件。实践中，使用减压的滞后时间影响碳酸盐填料的粒度 (APS)。在测试中，0 微米是指纸浆中未制造碳酸盐填料。6.5 和 13 微米的碳酸盐填料粒度分别对应于在 0.92 巴的减压和 45° 的温度下的 40 秒 (100 g CaO/30 l)) 6.5 μm 和 600 秒 (200 g CaO/30 l)（13 μm）的滞后时间。

[0088] 为产生减压，使用 50 升钢容器，其中借助于泵形成减压。减压处理之前，根据实施

例 1，用碳酸氢盐离子溶液将添加了期望部分的淀粉的 3.8% 纸浆稀释到 0.2% 的稠度。

[0089] 测试中所用的阳离子纸浆淀粉来自 Chemigate Oy (Raisamyl，其 DS 为 0.035)。每次使用时，在 1 分钟混合时间处将纸浆淀粉加入 3.8% 纸浆，然后将其稀释到 0.2% 的稠度。将高岭土 (Capim 和 Intramax) 加入 0.2% 纸浆。根据实施例 1 制造的碳酸氢盐离子溶液用于将纸浆从 3.8% 稀释到 0.2%。通过减压由该纸浆制造碳酸盐填料。作为助留剂，在混合期间将 200 g/t PAM (Fennopol 3400, Kemira) 加入薄板模具。

[0090] 表 4 中示出测试计划的测试点。

[0091] 表 4. 测试计划的条件。将淀粉加入 3.8% 纸浆，然后将其稀释到 0.2%。

测试	淀粉，kg/t	碳酸盐的粒度，μm	gCaO/30l	减压，巴	温度，℃
1	0	0	0	未使用	未使用
2	10	13	200	0.92	45
3	5	6.5	100	0.92	45
4	0	13	200	0.92	45
5	5	6.5	100	0.92	45
6	10	0	0	未使用	未使用
7	5	6.5	100	0.92	45

[0092] 整体看来，测试计划极其成功。最终模型的确定指数高于 95%。按史考特粘结值和 TEA 值来测量强度。测量的光学值包括不透明度和亮度 (ISO)。自然地，强度 (Scott & TEA) 受纸浆淀粉的部分影响，10 kg/t 产生最佳强度水平。碳酸盐填料的粒度 (APS) 本身 (但尤其是与淀粉部分一起) 对强度具有明显相互作用。这意味着碳酸盐填料可以用于积极影响淀粉部分的减少和强度的维持，即使网络中填料的量增加。

[0093] 图 1 表明出当碳酸盐填料的粒度为约 6.5 微米并且纸浆淀粉的量为 5 kg/t 时实现最佳 TEA 强度。在对照点处实现的对应 TEA 强度 (J/m^2) 为：

对照 1 54

对照 2 70

对照 3 90。

[0094] 图 2 表明 10 kg/t 的淀粉部分和无碳酸盐填料产生最佳史考特粘结强度。在对照点处实现的对应史考特粘结强度 (J/m^2) 为：

对照 1 214

对照 2 302

对照 3 324。

[0095] 在 80 g/m^2 的基重和 10% 的填料含量下，用 Capim SBF、Intramax 和根据本发明的碳酸盐填料实现的强度示于表 5 中。

[0096] 表 5. 所用的高岭土和碳酸盐填料产生这些 TEA 值和史考特粘结值。对于高岭土，10 kg/t，并且对于碳酸盐填料 (APS 6.5 μm)，5 kg/t。

填料	TEA, J/m2	史考特粘结值, J/m2

Intramax	44	211
Capim	46	208
碳酸盐填料	77	273

[0097] 如上所述，使用 10 kg/t 的纸浆淀粉实现上述值。当使用 6.5 μm 的碳酸盐填料和 5 kg/t 的纸浆淀粉时，实现 273 J/m^2 的史考特粘结强度和 77 J/m^2 的 TEA 强度。两值明显高于高岭土填料的对应量（表 5）。来自无填料纸浆的 5 kg/t 的纸浆淀粉产生 302 J/m^2 的史考特粘结强度，所以具有此量淀粉的碳酸盐填料导致的最大强度降低是次要的。

[0098] 在淀粉部分和碳酸盐填料的粒度之间，存在对强度的强烈相互影响。对于相互作用，测试计划的 P 值为 0.01。低于 0.05 的 P 值意味着淀粉部分和碳酸盐填料的粒度对强度具有强烈相互作用。单独就统计学而言，淀粉部分和碳酸盐填料的粒度对强度具有显著影响。

[0099] 使用该碳酸盐填料，可以实现与高岭土之一相比，有所改善的不透明度和亮度组合，如图 3 所指示。当针对高岭土的表 5 的结果和用由该测试计划获得的 50% 的较小量纸浆淀粉改善的强度性质添加于此时，显而易见的是，碳酸盐填料单独（以及尤其与淀粉一起）向纸张或纸板制造商提供用该填料实现优良光学性质并同时维持改善的强度性质的机会。

[0100] 图 4 示出在 80 g/m^2 的所制造化学纸浆薄板的表面上各粒度级别（6.5 和 13 μm）的碳酸盐粒子。在图中，可以观察到碳酸盐填料的棱角形状。在下行 6.5 μm 的碳酸盐填料中，也可以观察碳酸盐填料的结构中的孔隙度。图 4 还示出碳酸盐填料如何清晰粘结到纤维物质（淀粉和 / 或纤维的小纤维）。

[0101] 实施例 4（用另一种矿物填料沉淀碳酸氢盐）

在此测试系列中，0、10% 和 20% 的研磨碳酸钙 GCC（由干燥纤维计算）加入前述实例的 3.8% 纸浆作为对照样品 (Hydrocarb 60 Filler LV, Omya)。作为对照样品，还使用沉淀碳酸钙 PCC (FS-240, Shaefer Finland Oy)。从对照样品获得的光学（亮度和不透明度）性质和强度（史考特粘结）与根据前述实例制造和使用减压获得的结果比较。在此实例中，如下进行减压：首先，将 5 kg/t 淀粉 (Raisamyl DS 0.035; Chemigate Oy) 加入 3.8% 纸浆。此后，用碳酸氢盐离子溶液将 3.8% 纸浆稀释到 0.2% 稠度，并且随后，将 10% 或 20% GCC 或 PCC 加入此稀释纸浆，同时均匀搅拌，然后减压。表 5 中这些测试点称为 GCC 和 PCC 减压，其中示出归一化至 5% 填料含量的结果。通过将 100 g 氧化钙加入 30 升所制造溶液，根据实施例 1 制造碳酸氢盐离子溶液。对用碳酸氢盐离子溶液稀释的 0.2% 纤维纸浆和 10% 或 20% 的 GCC 或 PCC 进行减压。此后，将该混合物保持在 0.92 巴的减压下 40 秒。在对照点 (GCC 和 PCC)，也将 5 kg/t 淀粉加入 3.8% 纸浆。此后，用自来水将纸浆稀释到 0.2% 的稠度。制作薄板之前，将 10% 或 20% 的 GCC 或 PCC 加入此稀释纸浆。作为助留剂，在混合期间将 200 g/t PAM (Fennopol 3400, Kemira) 加入薄板模具。

[0102] 由如此制造的约 0.2% 稠度的纸浆，根据标准 SCAN-C 26:76 (SCAN-M 5:76)，不用循环水，在薄板模具中生产 80 g/m^2 的薄板（来自各测试点的 10 个薄板）。此后，薄板在鼓式干燥器中 105℃下干燥两个小时，然后将它们取出在 23℃和相对湿度 50% 下吹风 48 小时。此后，核实它们的基重并且测定以下性质：

- 填料含量 (525℃，2 小时）
- ISO 亮度 (L&W Elrepho 分光光度计 SE070), ISO 2470
- 不透明度 (L&W Elrepho 分光光度计 SE070), ISO 2471

• 史考特粘结值（内部粘结测试仪 Huygen)，Tappi-UM403

• 厚度 (L&W 厚度测试仪 SE51)， ISO 534

薄板的基重处于 80 g/m^2 的目标基重处，并且精确度为 ±0.6 g/m^2。

[0103] 通过测量密度，评估此测试中薄板的印刷性质。在薄板的上表面上用 10 毫克油墨通过使用 Cold set black (Sun Chemical，粘度 7.3 Pas)，通过 Universial Testprinter (Testprint B.V.)，印刷薄板。印刷后 24 小时，由被吹风且干燥的样品通过密度计 (Macbeth) 测量密度。Universial testprinter 使用 630 N 的压力和 1 m/s 速度。

[0104] 根据由薄板确定 (525℃和 2 小时）的填料含量，结果归一化至 5% 的相同填料含量。在表 6 中，示出结果，归一化至 5% 的填料含量。95% 是指 95% 的置信区间。

[0105] 表 6. 以 80 g/m^2 的基重归一化至 5% 的填料含量的测试结果。

测试点	不透明度，%	亮度，%	史考特粘结值，J/m2	厚度，μm	光密度，10g
GCC	83.2	84.7	185	163	1.43
PCC	84.6	85.5	182	186	1.46
GCC 减压	86.4	88.1	255	229	1.72
PCC 减压	86.2	88.3	246	226	1.69
95%	±0.5	±0.3	±9	±8	±0.06

[0106] 表 6 的结果指示，在 GCC 和 PCC 减压点以及对照点 GCC 和 PCC 处强度（史考特粘结）、光学值（亮度和不透明度）、厚度和光密度均处于改善水平。

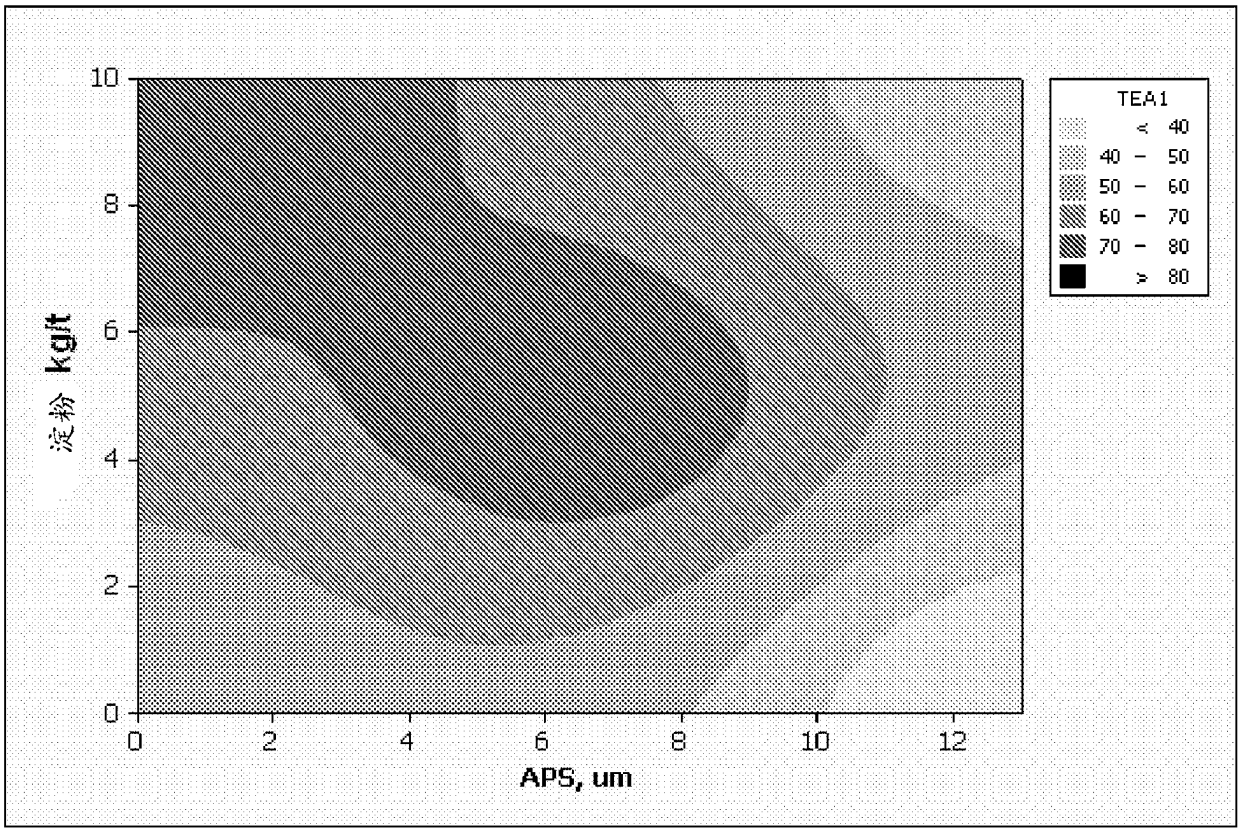
10
8
6
4
2
0
淀粉 kg/t
0
2
4
6
8
10
12
APS, um
TEA1
< 40
40 - 50
50 - 60
60 - 70
70 - 80
> 80

图 1

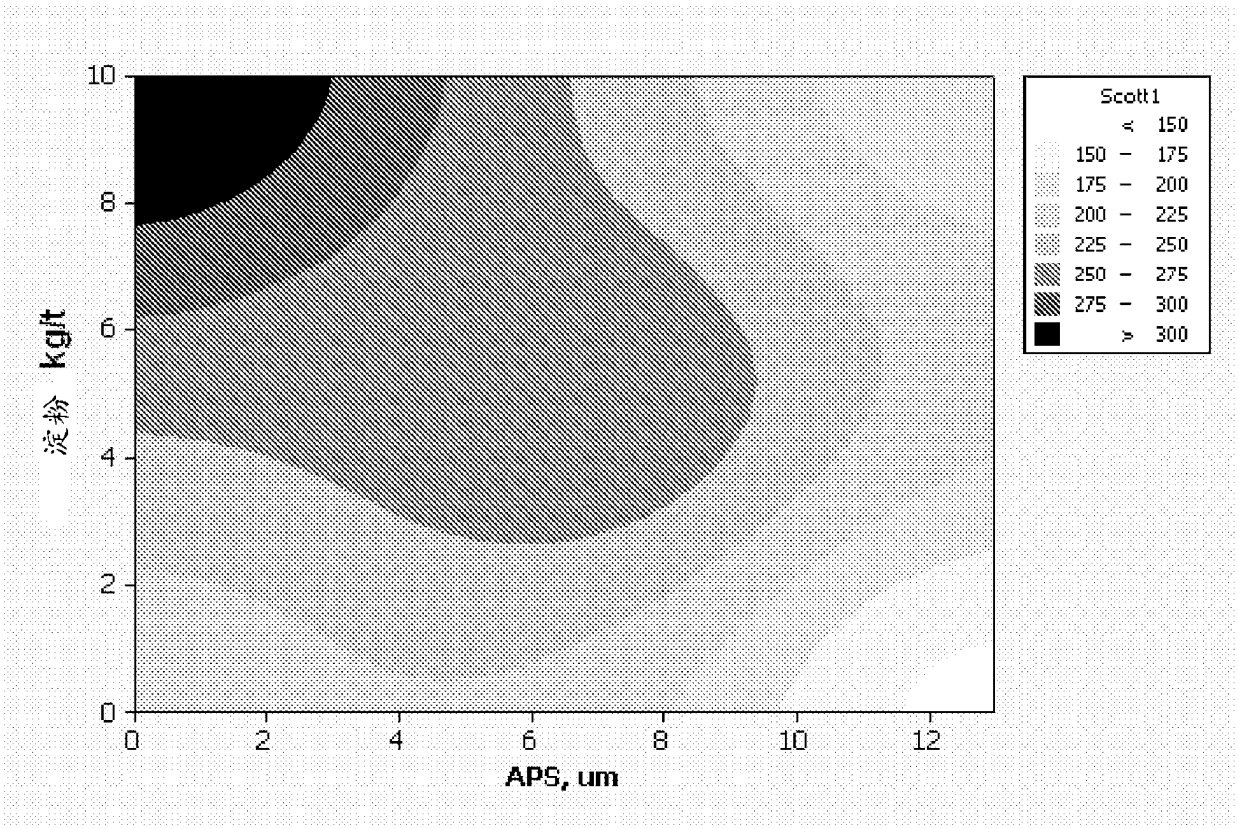
Scott1
≤ 150
150 – 175
175 – 200
200 – 225
225 – 250
250 – 275
275 – 300
≥ 300
淀粉 kg/t
APS, um
0
2
4
6
8
10
12

图 2

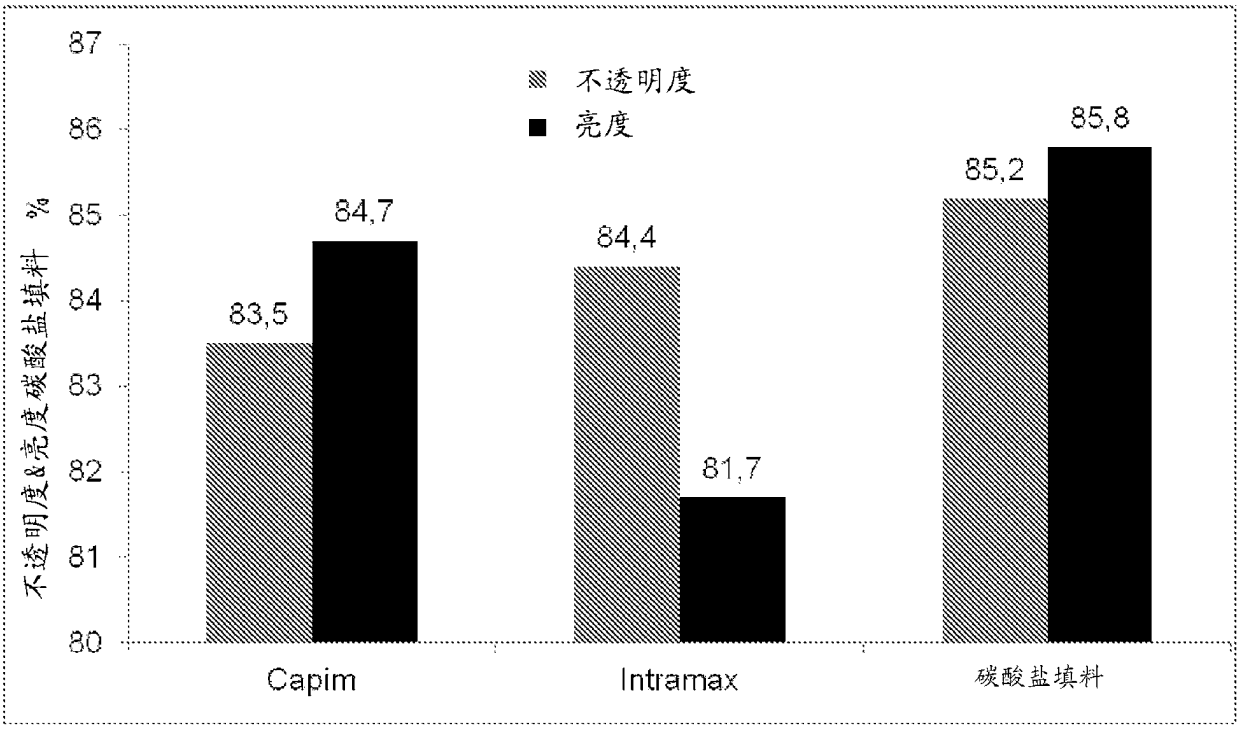
不透明度
亮度
不透明度&亮度碳酸盐填料 %
87
86
85
84
83
82
81
80
83,5
84,7
84,4
81,7
85,2
85,8
Capim
Intramax
碳酸盐填料

图 3

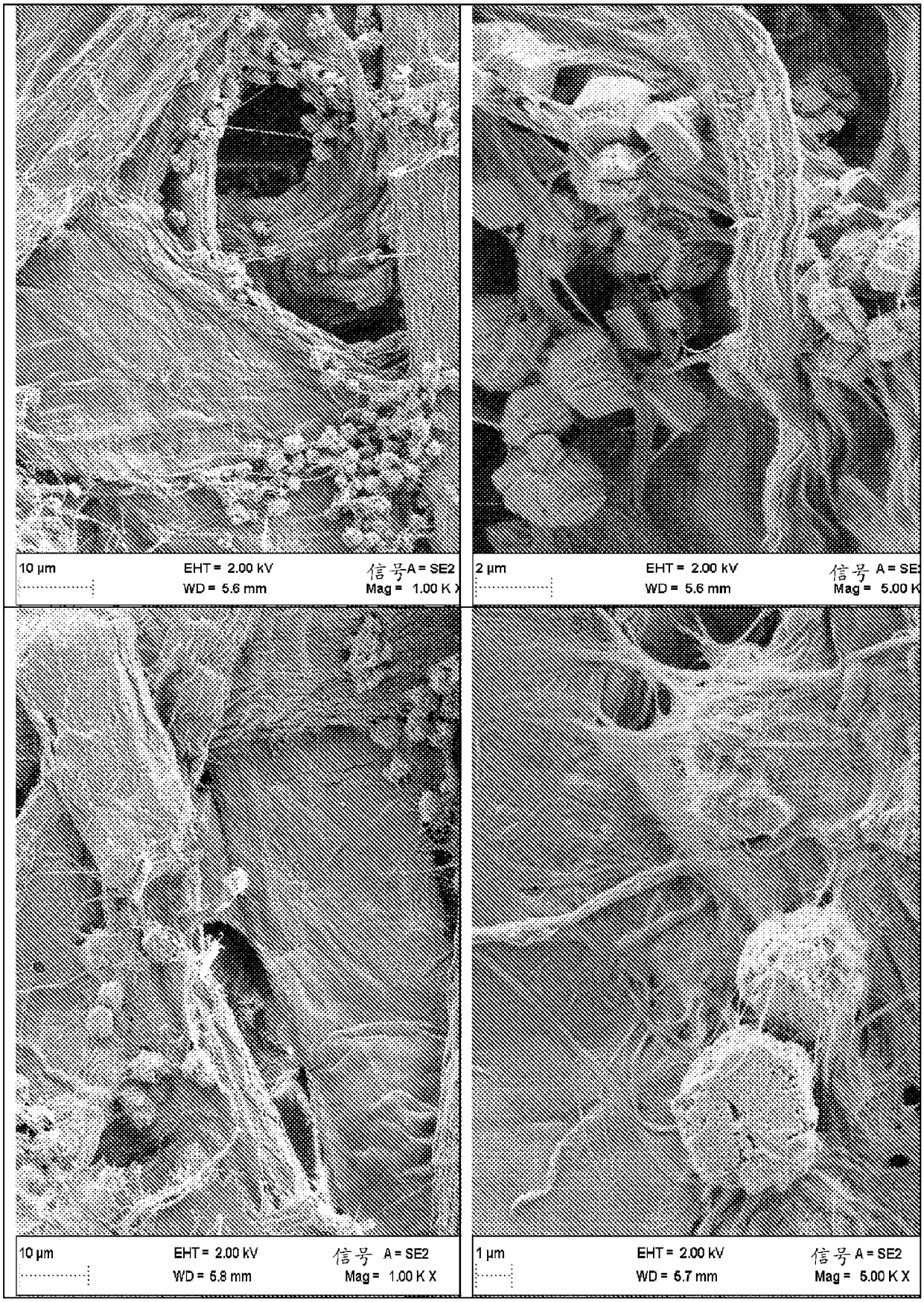
10 µm
EHT = 2.00 kV
WD = 5.6 mm
信号A = SE2
Mag = 1.00 K X
2 µm
EHT = 2.00 kV
WD = 5.6 mm
Mag = 5.00 K
10 µm
EHT = 2.00 kV
WD = 5.8 mm
信号 A = SE2
Mag = 1.00 K X
1 µm
EHT = 2.00 kV
WD = 5.7 mm
信号 A = SE2
Mag = 5.00 K X

图 4