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**(54) FILLER FOR PAPERMAKING PROCESS**

FÜLLSTOFF FÜR PAPIERHERSTELLUNG

CHARGE UTILISEE DANS LA FABRICATION DU PAPIER

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**Description**

**[0001]** The present invention relates to a filler comprising calcium salt and cellulose derivative. The invention further relates to a method of making the filler, the use of the filler in papermaking, a process for papermaking in which the filler is used as an additive as well as paper comprising the filler.

Background of the Invention

**[0002]** Highly filled paper is an established trend in the paper industry not only due to the savings in the decreased use of fibre, but also due to improved product quality, such as higher opacity and better printability. Calcium carbonate-based fillers are commonly used, because of their superior light scattering properties. A major drawback in the production of highly filled paper, particularly with fillers having high surface area, is the high consumption of sizing agent. Thus, as the content of filler in the paper increases, a larger amount of sizing agent is required in order to obtain corresponding sizing results. Hence, cellulosic suspensions are more difficult to size when the amount of filler increases.

**[0003]** Sizing is primarily performed in order to achieve water repellence in paper or board and reduce edge wicking. It will also affect mechanical properties of paper and board, such as dimensional stability, friction coefficient, pliability and folding endurance. Additionally, sizing may improve printability specifically by controlling ink spreading and adhesion.

**[0004]** The sizing process involves the deposition of hydrophobic substances, commonly referred to as sizing agents, on the fibre surface. Commonly employed sizing agents are non-cellulose-reactive sizing agents, e.g. rosin-based sizing agents, and cellulose-reactive sizing agents, e.g. alkyl ketene dimers ("AKD") and acid anhydrides such as alkenyl succinic anhydride ("ASA"). It is known, however, that cellulose-reactive sizing agents, i.e. AKD and ASA, undergo hydrolysis that competes with the desired reaction with the fibres. Moreover, sizing losses in the final product can occur due to size inversion or migration, size evaporation, mechanical wear of the product, etc.

**[0005]** Bartz and co-workers have observed that during increased fluidity of AKD wax, some AKD could penetrate and thereafter be trapped in the pore structure of the filler (Bartz, W.; Darroch, M.E.; Kurrle, F.L., "Alkyl ketene dimer sizing efficiency and reversion in calcium carbonate filled papers", Tappi Journal, Vol. 77, No. 12, 1994). This occurs particularly with the scalenohedral form of PCC, which has the porous rosette structure and high surface area. Voutilainen has shown that fillers with high surface area adsorb AKD even better than fibres (Voutilainen, P., "Competitive Adsorption of Alkyl Ketene Dimer on Pulp Fibers and CaCO<sub>3</sub> Fillers", Proceedings from International Paper and Coating Chemistry Symposium, 1996). The presence of Al- and Si-oxides on the filler surface may additionally adsorb cationic starch contained in the AKD particles. It has also been proposed that a strong interaction, or perhaps even bonding, exists between AKD and calcium carbonate filler. These proposed mechanisms with the filler are naturally undesired, and efforts should be made to minimise these interaction.

**[0006]** To improve sizing efficiency, it is suggested in U.S. Patent No. 5,514,212 that the surface of the pigment can be modified with an anionic starch-soap complex. Cooked starch from corn or potato is complexed with fatty acid salts and precipitated onto pigment surfaces when mixed with precipitated calcium slurry or papermaking furnish containing high levels of calcium ions.

**[0007]** U.S. Patent No. 5,972,100 suggests a system consisting of a cellulose-reactive size (such as AKD), a cationic dispersing agent (such as cationic starch or polyamides) and a filler. Aside from improved sizing, the invention allows independent control of both filler loading and sizing separately.

**[0008]** Furthermore, WO 95/13324 refers to calcium carbonate treated with a cellulose derivative such as sodium carboxymethyl cellulose ("CMC") having a degree of substitution of 0.7. Said treated calcium carbonate is used as filler in alkaline papermaking suspensions whereby the brightness of the paper is increased.

**[0009]** U.S. Patent No. 3,730,830 discloses a process for making paper, specifically photographic paper, comprising the use of synthetic polymer fibres. Prior to the addition of the synthetic fibres to the fibre suspension, inorganic pigment or carbon is added to a slurry containing carboxymethyl cellulose and the synthetic fibres thereby achieving uniform dispersion of the polymer fibres among the cellulose fibres in the paper stock.

**[0010]** WO 02/086238 discloses a filler for paper comprising specific cellulose material. The use of a cellulose derivative of the invention is not disclosed or suggested.

**[0011]** EP 0 758 695 A discloses the use of fibrous cellulose to make water-dispersible paper sheets. There is no disclosure or suggestion to use a cellulose material according to the invention.

**[0012]** US 5,492,560 discloses to use a specific carboxymethyl cellulose to treat an inorganic filler. The use of a cellulose material of the invention is not disclosed or suggested.

**[0013]** US 2003/188738 discloses that anionic co-additives can be used in papermaking. Carboxymethyl cellulose is mentioned as a possible co-additive. There is no disclosure or suggestion to use a cellulose material according to the invention.

**[0014]** There is still a need for a filler which provides an improved papermaking process and better properties of the paper produced. It would be desirable to provide a filler which renders possible production of highly filled paper showing

excellent printing and mechanical properties. It would also be desirable to provide a filler which reduces the sizing demand and hereby results in improved sizing efficiency. It would also be desirable to provide a filler that is compatible with drainage and retention aids, and hereby leads to good drainage, retention and paper machine runnability, It would also be desirable to provide a simple and efficient process for producing a filler showing the above characteristics.

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### Summary of the Invention

**[0015]** The present invention generally relates to a filler comprising calcium salt and an amphoteric cellulose derivative. The present invention further generally relates to a filler comprising calcium salt and an amphoteric carboxyalkyl cellulose derivative. The invention also generally relates to a method of making the filler by mixing a calcium salt-containing material with a cellulose derivative, the use of the filler as an additive in papermaking as well as paper comprising the filler. The invention further generally relates to a papermaking process in which the filler is introduced into an aqueous cellulosic suspension.

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**[0016]** More specifically, the invention relates to a filler according to claim 1. The invention further relates to a method of producing a filler which comprises mixing a calcium salt-containing material with an amphoteric cellulose derivative according to claim 1. The invention further relates to a filler obtainable by these methods. The invention further relates to a papermaking process which comprises providing an aqueous suspension containing cellulosic fibres, introducing into the suspension a filler comprising calcium salt and an amphoteric cellulose derivative according to claim 1, and dewatering the suspension to form a web or sheet of paper. In the papermaking process, the filler can be introduced into the cellulosic suspension by adding the calcium salt and cellulose derivative together as a single composition.

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### Detailed Description of the Invention

**[0017]** The present invention provides a new filler that is suitable for use in papermaking. It has surprisingly been found that the filler according to the invention makes it possible to reduce some of the problems associated with fillers commonly used in papermaking and incorporated in paper. More specifically, by employing the filler of this invention in papermaking processes it is possible to provide paper with excellent printing properties, e.g. high smoothness, high opacity and whiteness, improved mechanical properties, e.g. dry strength, tensile strength, Scott bond and bending stiffness, and improved sizing effect. Additional advantages shown by the present invention include good and/or improved dewatering and fines retention, which lead to benefits in terms of paper machine runnability.

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**[0018]** When using the filler in conjunction with a sizing agent, it has been observed that the present invention makes it possible to reduce the sizing demand and, thus, generally improving sizing efficiency. The improved sizing efficiency is exhibited for different types of sizing agents, including non-cellulose and cellulose-reactive sizing agents, specifically cellulose-reactive sizing agents such as ketene dimers and acid anhydrides. In particular, the invention provides improved sizing efficiency and sizing stability of filled paper, especially with high filler loading and/or when fillers with high surface areas are used.

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**[0019]** According to the present invention it has also been observed, unexpectedly, that the cellulose derivative can be mixed with and more effectively be adsorbed on or attached to the calcium salt-containing material during simple processing. The filler of the invention can be regarded as a modified filler, or cellulose derivative-treated filler.

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**[0020]** According to the present invention it has been found that very good results can be obtained by adding the calcium salt-containing material and amphoteric cellulose derivative to a cellulosic suspension together in a pre-mixed or pre-treated form. The pre-treatment of the calcium salt-containing material with the cellulose derivative provides a convenient way of separately processing only one component of the cellulosic suspension to produce a modified filler, which can be used instead of or partly replacing conventional filler. Without being bound by any theory, it is believed that the cellulose derivative is adsorbed to the calcium salt-containing material when mixing the components.

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**[0021]** The filler according to the invention comprises a calcium salt and an amphoteric cellulose derivative. Examples of suitable calcium salts include calcium carbonate, calcium sulphate and calcium oxalate, preferably calcium carbonate, and mixtures thereof. Calcium carbonate is the main constituent in limestone, marble, chalk and dolomite. Calcium carbonate can be obtained directly from the above mentioned naturally occurring species of stone and is then referred to as ground calcium carbonate ("GCC"). Calcium carbonate can also be synthetically produced, commonly referred to as precipitated calcium carbonate ("PCC"). The calcium carbonate is preferably obtained from calcium hydroxide and a material which produces carbonate ions in the aqueous phase, such as an alkali metal carbonate or carbon dioxide. Both GCC and PCC can be used in the present invention, preferably PCC, including any of the various crystalline forms or morphologies that exist, e.g. calcite of rhombohedral, prismatic, tabular, cuboid and scalenohedral forms and aragonite of acicular form. The PCC usually has a specific area of from about 2 to about 20 m<sup>2</sup>/g, suitably from about 7 to about 12 m<sup>2</sup>/g.

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**[0022]** The calcium salt can be present as essentially pure calcium salt, including mixtures of one or more calcium salts. It can also be present in the form of a mixture together with one or more other components. The term "calcium

salt-containing material", as used herein, refers to a material comprising calcium salt, and optionally one or more other components. Examples of suitable other components of this type include fibres or fibrils of cellulose, lignocellulose or similar vegetable materials, inorganic clays, kaolin, talc, titanium dioxide, hydrogenated aluminium oxides, barium sulphate, etc. Preferably, when used, the other components are suited for use in papermaking.

**[0023]** In calcium salt-containing materials comprising fibres or fibrils of cellulose, lignocellulose or similar vegetable materials, at least part of the calcium salt can be deposited on the fibres or fibrils. The average thickness of the fibrils can be from about 0.01 up to about 10  $\mu\text{m}$ , suitably up to about 5  $\mu\text{m}$  and preferably up to about 1  $\mu\text{m}$ . The average length of the fibrils can be from about 10  $\mu\text{m}$  up to about 1500  $\mu\text{m}$ . Examples of suitable calcium salt-containing materials include the composite materials disclosed in U.S. Patent Nos. 5,731,080; 5,824,364; 6,251,222; 6,375,794; and 6,599,391, commercially available composite materials of this type include SuperFill<sup>®</sup> of M-Real Oy.

**[0024]** The filler according to the invention further comprises an amphoteric cellulose derivative. It is preferred that the cellulose derivative is water-soluble or at least partly water-soluble or water-dispersible, preferably water-soluble or at least partly water-soluble. Preferably, the cellulose derivative is ionic. The cellulose derivative can be anionic and/or amphoteric. Examples of suitable cellulose derivatives include cellulose ethers, e.g. anionic and amphoteric cellulose ethers. The cellulose derivative preferably has ionic or charged groups, or substituents. Examples of suitable ionic groups include anionic and cationic groups. Examples of suitable anionic groups include carboxylate, e.g. carboxyalkyl, sulpho- nate, e.g. sulphonyl, phosphate and phosphonate groups in which the alkyl group can be methyl, ethyl propyl and mixtures thereof, suitably methyl; suitably the cellulose derivative contains an anionic group comprising a carboxylate group, e.g. a carboxyalkyl group. The counter-ion of the anionic group is usually an alkali metal or alkaline earth metal, suitably sodium.

**[0025]** Examples of suitable cationic groups of cellulose derivatives according to the invention include salts of amines, suitably salts of tertiary amines, and quaternary ammonium groups, preferably quaternary ammonium groups. The substituents attached to the nitrogen atom of amines and quaternary ammonium groups can be same or different and can be selected from alkyl, cycloalkyl, and alkoxyalkyl, groups, and one, two or more of the substituents together with the nitrogen atom can form a heterocyclic ring. The substituents independently of each other usually comprise from 1 to about 24 carbon atoms, preferably from 1 to about 8 carbon atoms. The nitrogen of the cationic group can be attached to the cellulose or derivative thereof by means of a chain of atoms which suitably comprises carbon and hydrogen atoms, and optionally O and/or N atoms. Usually the chain of atoms is an alkylene group with from 2 to 18 and suitably 2 to 8 carbon atoms, optionally interrupted or substituted by one or more heteroatoms, e.g. O or N such as alkyleneoxy group or hydroxy propylene group. Preferred cellulose derivatives containing cationic groups include those obtained by reacting cellulose or derivative thereof with a quaternization agent selected from 2, 3-epoxypropyl trimethyl ammonium chloride, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and mixtures thereof.

**[0026]** The cellulose derivatives of this invention can contain non-ionic groups such as alkyl or hydroxy alkyl groups, e.g. hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxybutyl and mixtures thereof, e.g. hydroxyethyl methyl, hydroxypropyl methyl, hydroxybutyl methyl, hydroxyethyl ethyl, hydroxypropyl and the like. In a preferred embodiment of the invention, the cellulose derivative contains both ionic groups and non-ionic groups.

**[0027]** According to a preferred embodiment of the invention the filler comprises a calcium salt containing fibres or fibrils of cellulose or lignocellulose and a cellulosic derivative containing cationic groups. The cationic groups can be any one of those listed in this application.

**[0028]** In another preferred embodiment of the invention the filler comprises a calcium salt which is substantially free from fibres or fibrils of cellulose or lignocellulose and an amphoteric cellulosic derivative.

**[0029]** The terms "degree of substitution" or "DS", as used herein, mean the number of substituted ring sites of the beta-anhydroglucose rings of the cellulose derivative. Since there are three hydroxyl groups on each anhydroglucose ring of the cellulose that are available for substitution, the maximum value of DS is 3.0. According to the invention, the net ionic substitution of the cellulose derivative is net anionic. When the net ionic substitution is net anionic, there is a net excess of anionic groups (net anionic groups = the average number of anionic groups minus the average number of cationic groups, if any, per glucose unit) and  $DS_{NI}$  (degree of substitution of net ionic groups) is the same as the degree of substitution of net anionic groups (" $DS_{NA}$ "). According to the invention,  $DS_{NA}$  is up to about 0.60, suitably up to about 0.50, preferably up to about 0.45 and more preferably up to 0.40, whereas  $DS_{NA}$  is at least 0.01, suitably at least about 0.05, preferably at least about 0.10 and more preferably at least about 0.15. The ranges of  $DS_{NA}$  are from about 0.01 to about 0.60, suitably from about 0.05 to about 0.50, preferably from about 0.10 to about 0.45 and more preferably from about 0.15 to about 0.40.

**[0030]** Cellulose derivatives that are amphoteric have a degree of anionic substitution (" $DS_A$ ") in the range of from 0.01 to about 1.0 as long as  $DS_{NI}$  and  $DS_{NA}$  are as defined herein; suitably from about 0.05, preferably from about 0.10, and more preferably from about 0.15 and suitably up to about 0.75, preferably up to about 0.5, and more preferably up to about 0.4. For amphoteric cellulose derivatives of this invention  $DS_A$  can of course be higher than 0.65 as long as  $DS_{NA}$  is as defined herein. For example, if  $DS_A$  is 0.75 and  $DS_C$  (degree of cationic substitution) is 0.15, then  $DS_{NA}$  is 0.60.

**[0031]** Examples of suitable cellulose derivatives having degrees of substitution as defined above include the water-

soluble low DS carboxyalkyl cellulose derivatives disclosed in copending patent applications filed in the name of Akzo Nobel N.V. of even date. The water-soluble cellulose derivatives suitably has a solubility of at least 85 % by weight, based on total weight of dry cellulose derivative, in an aqueous solution, preferably at least 90 % by weight, more preferably at least 95 % by weight, and most preferably at least 98 % by weight.

5 **[0032]** The cellulose derivative usually has an average molecular weight which is at least 20,000 Dalton, preferably at least 50,000 Dalton, and the average molecular weight is usually up to 1,000,000 Dalton, preferably up to 500,000 Dalton.

10 **[0033]** Preferably, in the filler according to the invention, the cellulose derivative is at least in part adsorbed on or attached to the calcium salt or other components present in the calcium salt-containing material. Suitably, at least about 10 % by weight, preferably at least about 30 % by weight, more preferably at least about 45 % by weight and most preferably at least about 60 % by weight of the cellulose derivative is adsorbed on or attached to the calcium salt or other components present in the calcium salt-containing material.

15 **[0034]** The filler according to the invention usually has a calcium salt content of at least 0.0001 % by weight; the calcium salt content can be from about 0.0001 to about 99.5 % by weight, suitably from about 0.1 to about 90 % by weight, and preferably from about 60 to about 80 % by weight, based on the weight of the solids of the filler, i.e. based on the dry weight of the filler. The filler usually has a cellulose derivative content of at least 0.01 % by weight; the cellulose derivative content can be from about 0.01 to about 30 % by weight, suitably from about 0.1 to about 20 % by weight, and preferably from about 0.3 to about 10 % by weight, based on the weight of the solids of the filler.

20 **[0035]** The filler according to the invention can be supplied as a solid material that can be essentially free of water. It can also be supplied as an aqueous composition. The content of aqueous phase, or water, can vary within wide limits, depending on the method of production and intended use.

25 **[0036]** The present invention also relates to a method of making a filler which comprises mixing an amphoteric cellulose derivative, e.g. any one of the cellulose derivatives defined herein, with a calcium salt-containing material, e.g. any one of the calcium salt-containing materials defined herein, which comprises calcium salt, and optionally one or more other components. The cellulose derivative and calcium salt-containing material are suitably used in amounts so as to provide a filler according to the invention having contents of cellulose derivative and calcium salt as defined herein.

30 **[0037]** The cellulose derivative and calcium salt-containing material used can be present as solids or in aqueous compositions, and mixtures thereof. The calcium salt-containing material is suitably present as a finely divided material. The mixing can be achieved by adding the cellulose derivative to the filler, or vice versa, in a batch, semi-batch or continuous process. According to a preferred embodiment of the invention, the cellulose derivative is added as a solid to an aqueous composition of the calcium salt-containing material and the composition obtained is then suitably subjected to effective dispersing to dissolve the cellulose derivative. Preferably, the mixing is carried out by first forming a neutral to alkaline aqueous phase, suitably an aqueous solution, of cellulose derivative which is then mixed with an aqueous composition of calcium salt-containing material. Prior to mixing with the calcium salt-containing material, the aqueous phase of cellulose derivative can be subjected to pre-treatment, e.g. homogenisation, centrifugation and/or filtration, for example for separating undissolved cellulose derivative, if any, from the aqueous phase.

35 **[0038]** Preferably, the cellulose derivative is mixed with the calcium salt-containing material to allow at least part of the cellulose derivative to adsorb on or attach to the calcium salt-containing material, preferably so that it is hardly removed from the material by dilution with water. This can be accomplished by carrying out mixing under a period of time that is sufficient long to allow the adsorption on attachment. Suitably the mixing time is at least about 1 min, preferably at least about 5 min, more preferably at least about 10 min and most preferably at least about 20 min. Mixing periods of even several hours (1 - 10 h) are possible if it is desired to reach a high degree of attachment. Suitably, at least about 10 % by weight, preferably at least about 30 % by weight, more preferably at least about 45 % by weight and most preferably at least about 60 % by weight of the cellulose derivative is transferred from the aqueous phase and adsorbed on or attached to the calcium salt or other components present in the calcium salt-containing material.

45 **[0039]** The pH of the aqueous phase of cellulose derivative is usually adjusted for sorption of the specific cellulose derivative used at a value from about 4 to about 13, preferably from about 6 to about 10, more preferably from about 7 to about 8.5. A suitable base or acid can be used for adjusting the pH. Examples of suitable bases include bicarbonates and carbonates of alkali metals and alkali metal hydroxides, suitably sodium bicarbonate, sodium carbonate and sodium hydroxide. Examples of suitable acids include mineral acids, organic acids and acid salts, suitably sulphuric acid and its acid salts, such as alum. In general, at a lower pH, i.e. a pH from about 4.0 to neutral, adsorption of the cellulose derivative is higher but solubility is decreased, whereas at higher pH the adsorption is reduced but solubility is increased.

50 **[0040]** The temperature is not critical; in operations in non-pressurized conditions the temperature is typically from about 10 to about 100 °C, preferably from about 20 to about 80 °C. However, higher temperatures are more favourable, suitably the temperature of the aqueous composition during mixing is from about 30 up to about 70 °C, more preferably from about 40 up to about 60 °C.

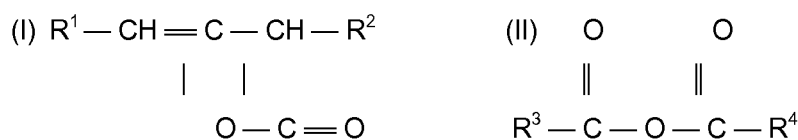
55 **[0041]** When using calcium salt-containing material also containing other components than calcium salt, e.g. fibres or fibrils of cellulose or lignocellulose, the mixing and attaching of cellulose derivative can be done simultaneously with

precipitation of the calcium salt on the fibrils or fibres or after the precipitation. It is also possible to add the cellulose derivative before the precipitation. In that case the cellulose derivative is added either during beating or in a separate sorption after beating. The cellulose derivative can be adsorbed on or attached to the calcium salt-containing material or fibre or fibril surfaces and/or sorbed into the fibres or fibrils. Methods of adsorbing similar cellulose derivatives to similar filler materials are disclosed in U.S. Patent Nos. 5,731,080; 5,824,364; 6,251,222; 6,375,794; and 6,599,391. The filler obtained by the method of the invention can be used as such, for example in papermaking. If present as an aqueous composition, it can be used directly or it can be dried, if desired, for example to simplify shipping.

**[0042]** The present invention also relates to a process for the production of paper which comprises providing an aqueous suspension containing cellulosic fibres ("cellulosic suspension"), introducing into the cellulosic suspension a filler, e.g. any one of the fillers defined herein, and dewatering the cellulosic suspension to form a web or sheet of paper. Preferably, the filler is introduced into the cellulosic suspension by adding it as a single composition. Alternatively, the calcium salt, or calcium salt-containing material (e.g. any one of the calcium salt-containing materials defined herein), and amphoteric cellulose derivative (e.g. any one of the cellulose derivatives defined herein) can be separately added to the cellulosic suspension and the filler is formed *in situ* in the cellulosic suspension.

**[0043]** In the process, other components may of course be introduced into the cellulosic suspension. Examples of such components include conventional fillers, optical brightening agents, sizing agents, drainage and retention aids, dry strength agents, wet strength agents, etc. Examples of suitable conventional fillers include kaolin, china clay, titanium dioxide, gypsum, talc, natural and synthetic calcium carbonates, e.g. chalk, ground marble and precipitated calcium carbonate, hydrogenated aluminum oxides (aluminum trihydroxides), calcium sulphate, barium sulphate, calcium oxalate, etc. When using the filler according to the invention together with conventional filler, the filler according to the invention can be present in an amount of at least 1 % by weight, suitably at least 5 % by weight, preferably at least 10 % by weight, more preferable at least about 20 % by weight, and suitably up to about 99 % by weight, based on the dry weight of all fillers. Examples of suitable sizing agents include non-cellulose-reactive sizing agents, e.g. rosin-based sizing agents like rosin-based soaps, rosin-based emulsions/dispersions, and cellulose-reactive sizing agents, e.g. emulsions/dispersions of acid anhydrides like alkenyl succinic anhydrides (ASA), alkenyl and alkyl ketene dimers (AKD) and multimers. Examples of suitable drainage and retention aids include organic polymeric products, e.g. cationic, anionic and non-ionic polymers including cationic polyethylene imines, cationic, anionic and non-ionic polyacrylamides, cationic polyamines, cationic starch, and cationic guar; inorganic materials, e.g. aluminium compounds, anionic microparticulate materials like colloidal silica-based particles, clays of smectite type, e.g. bentonite, montmorillonite; colloidal alumina, and combinations thereof. Examples of suitable combinations of drainage and retention aids include cationic polymers and anionic microparticulate materials, e.g. cationic starch and anionic colloidal silica-based particles, cationic polyacrylamide and anionic colloidal silica-based particles as well as cationic polyacrylamide and bentonite or montmorillonite. Examples of suitable wet strength agents include polyamines and polyaminoamides. Paper containing filler according to the invention and cationic starch shows very good strength properties.

**[0044]** According to a preferred embodiment of the invention, at least one sizing agent is introduced into the cellulosic suspension to produce sized paper containing filler. Preferably, the sizing agents are cellulose-reactive sizing agents of the types mentioned herein. Suitable ketene dimers have the general formula (I) below, wherein R<sup>1</sup> and R<sup>2</sup> represent saturated or unsaturated hydrocarbon groups, usually saturated hydrocarbons, the hydrocarbon groups suitably having from 8 to 36 carbon atoms, usually being straight or branched chain alkyl groups having 12 to 20 carbon atoms, such as hexadecyl and octadecyl groups. The ketene dimers may be liquid at ambient temperature, i.e. at 25 °C, suitably at 20 °C. Commonly, acid anhydrides can be characterized by the general formula (II) below, wherein R<sup>3</sup> and R<sup>4</sup> can be identical or different and represent saturated or unsaturated hydrocarbon groups suitably containing from 8 to 30 carbon atoms, or R<sup>3</sup> and R<sup>4</sup> together with the -C-O-C- moiety can form a 5 to 6 membered ring, optionally being further substituted with hydrocarbon groups containing up to 30 carbon atoms. Examples of acid anhydrides which are used commercially include alkyl and alkenyl succinic anhydrides and particularly isooctadecenyl succinic anhydride.



**[0045]** Suitable ketene dimers, acid anhydrides and organic isocyanates include the compounds disclosed in U.S. Pat. No. 4,522,686. The filler according to the invention can be added to the cellulosic suspension in amounts which can vary within wide limits depending on, inter alia, type of cellulosic suspension, type of paper produced, point of addition, etc. The filler is usually added in an amount within the range of from 1 to about 50 % by weight, suitably from about 5 to about 40 % by weight, and usually from about 10 to about 30 % by weight, based on the weight of dry fibres. Accordingly, the paper according to the invention usually has a content of filler of this invention within the range of from

1 to about 50 % by weight, suitably from about 5 to about 40 % by weight, and usually from about 10 to about 30 % by weight, based on the weight of dry fibres.

**[0046]** When using other components in the process, these components can be added to the cellulosic suspension in amounts which can vary within wide limits depending on, inter alia, type and number of components, type of cellulosic suspension, filler content, type of paper produced, point of addition, etc. Sizing agents are usually introduced into the cellulosic suspension in an amount of at least about 0.01 % by weight, suitably at least about 0.1 % by weight, based on the weight of dry fibres, and the upper limit is usually about 2 % by weight, suitably about 0.5 % by weight. Generally, drainage and retention aids are introduced into the cellulosic suspension in amounts that give better drainage and/or retention than what is obtained when not using these aids. Drainage and retention aids, dry strength agents and wet strength agents, independently of each other, are usually introduced in an amount of at least about 0.001% by weight, often at least about 0.005% by weight, based on dry fibres, and the upper limit is usually about 5% and suitably about 1.5% by weight. The term "paper", as used herein, include not only paper and the production thereof, but also other cellulosic fibre-containing sheet or web-like products, such as for example board and paperboard, and the production thereof. The process can be used in the production of paper from different types of aqueous suspensions of cellulosic (cellulose-containing) fibres and the suspensions should suitably contain at least 25% by weight and preferably at least 50% by weight of such fibres, based on a dry substance. The cellulosic fibres can be based on virgin fibres and/or recycled fibres, including fibres of wood or annual or perennial plants. The cellulosic suspension can be wood-containing or wood-free, and it can be based on fibres from chemical pulp such as sulphate, sulphite and organosolve pulps, mechanical pulp such as thermo-mechanical pulp, chemo-thermo-mechanical pulp, refiner pulp and ground wood pulp, from both hardwood and softwood, and can also be based on recycled fibres, optionally from de-inked pulps, and mixtures thereof. The cellulosic suspension suitably has a pH in the neutral to alkaline range, e.g. from about 6 to about 10, preferably from about 6.5 to about 8.0.

**[0047]** The paper produced can be dried, coated and calendered. The paper can be coated with, for example, calcium carbonate, gypsum, aluminium silicate, kaolin, aluminium hydroxide, magnesium silicate, talc, titanium dioxide, barium sulphate, zinc oxide, synthetic pigment, and mixtures thereof.

**[0048]** The grammage of the paper produced can vary within wide limits depending on the type of paper produced; usually the grammage is within the range from about 20 to about 500 g/m<sup>2</sup>, suitably from about 30 to about 450 g/m<sup>2</sup>, and preferably from 30 to about 110 g/m<sup>2</sup>. Preferably, the invention is used for the production of uncoated and coated offset paper, electrophotography paper, uncoated and coated fine paper, optionally containing mechanical pulp, as well as writing and printing papers. An especially preferred product is coated offset paper in which high gloss and high opacity and bulk are combined.

**[0049]** The invention is further illustrated in the following Examples which, however, are not intended to limit the same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

#### Example 1

**[0050]** Fillers according to the invention and for comparison were prepared by treating calcium salt-containing material with cellulose derivatives. Cellulose derivatives used were carboxymethyl celluloses ("CMC") having DS<sub>NI</sub> (DS<sub>CA</sub> = DS<sub>CM</sub> = DS<sub>A</sub> = DS<sub>NA</sub> = DS<sub>NI</sub>) of 0.3, 0.32 and 0.7, respectively. Another CMC used was quaternary ammonium carboxymethyl celluloses ("QN-CMC") having DS<sub>CA</sub> = DS<sub>CM</sub> = DS<sub>A</sub> = 0.4; DS<sub>C</sub> = DS<sub>QN</sub> = 0.17; and DS<sub>NI</sub> = DS<sub>NA</sub> = 0.4 - 0.17 = 0.23. The average molecular weights of the cellulose derivatives used were in the range of from 100,000 to 400,000.. Calcium salt-containing materials used were different precipitated calcium carbonates ("PCC") having a surface area of 5.7 and 10.0 m<sup>2</sup>/g, respectively. Another calcium salt-containing material used was SuperFill<sup>®</sup> (PCC on pulp fines).

**[0051]** The fillers were prepared by dissolving CMC into water to a consistency of 0.5 % by weight. Thereafter, the obtained CMC composition was added to PCC filler slurry and mixed during 25 to 45 minutes at a temperature of about 50 °C. The fillers according to the invention ("Invention Product") and for comparison ("Comparison Product") were the following:

Comparison Product 1 ("ICP1"):	CMC (DS <sub>NI</sub> 0.3)-treated PCC (5.7 m <sup>2</sup> /g)
Comparison Product 2 ("ICP2"):	CMC (DS <sub>NI</sub> 0.3)-treated PCC (10 m <sup>2</sup> /g)
Comparison Product 3 ("ICP3"):	CMC (DS <sub>NI</sub> 0.32)-treated SuperFill <sup>®</sup>
Invention Product 4 ("IP4"):	QN-CMC (DS <sub>NI</sub> 0.23)-treated SuperFill <sup>®</sup> .
Comparison Product 1 ("CP1"):	CMC (DS <sub>NI</sub> 0.7)-treated PCC (5.7 m <sup>2</sup> /g)
Comparison Product 1 ("CP2"):	SuperFill <sup>®</sup> .

Example 2

[0052] Sizing of paper produced according to the invention was evaluated and compared to paper used for comparison purposes. Paper was produced using ICP1 according to Example 1. Paper used for comparison was produced using CP1 according to Example 1 and using filler containing no cellulose derivative.

[0053] Paper sheets were produced from pulp consisting of chemical pulp and containing untreated PCC in varying amounts (% by weight, based on dry paper), as indicated in Table 1. To the pulp suspension was added 2.0 kg/tonne dry fibres of filler according to Example 1 and filler containing no cellulose derivative; 3.0 kg/tonne dry fibres of AKD (aqueous dispersion Eka Keydime C223), and a retention system comprising cationic starch (Eka PL 1510) and silica particles (Eka NP 780). Both the cationic starch and silica particles were added in an amount of 0.15 kg/tonne dry fibres. The addition sequence was as follows:

Addition of CMC-treated PCC:	0 sec
Addition of AKD dispersion:	30 sec.
Addition of cationic starch:	45 sec.
Addition of silica particles:	60 sec.
Sheet formation:	75 sec.

[0054] The sheets were made according to a standard method using a Dynamical Sheet Former ("Formette", CTP Grenoble). The Cobb<sub>60</sub> (SCAN-P 12:64) method was used in order to establish the sizing results. Table 1 shows the results obtained.

Table 1

Test No.	PCC Content of Paper	Filler	Cobb <sub>60</sub>
1	18 %	CP1	45
2	19 %	ICP1	25

Example 3

[0055] In this Example, papermaking processes were evaluated in which (i) CMC-treated PCC was added to the pulp suspension, and (ii) CMC and PCC (untreated) were separately added to the pulp suspension.

[0056] Paper sheets were produced from pulp of the same type used in Example 2 and containing 30 % by weight, based on dry paper, of untreated PCC (surface area of 10 m<sup>2</sup>/g) or CMC (DS<sub>NI</sub> 0.3)-treated PCC (10 m<sup>2</sup>/g) (ICP2 according to Example 1). To the pulp suspension was added 4 kg/tonne dry fibre of cationic starch (PB 970), 3.0 kg/tonne dry fibres of AKD (aqueous sizing dispersion Eka Keydime C223), and a retention system comprising cationic polyacrylamide (Eka PL 1310) and silica particles (Eka NP 780). Both the cationic polyacrylamide and silica particles were added in an amount of 0.20 kg/tonne dry paper. When untreated PCC was used, 1.0 kg/tonne of CMC having a DS<sub>NI</sub> of 0.3 was separately added. No separate addition of CMC was made when adding CMC-treated PCC. The addition sequence was as follows:

Addition of cationic starch:	0 sec
Addition of CMC-treated PCC / untreated PCC:	30 sec
Separate addition of CMC:	35 sec.
Addition of AKD:	45 sec.
Addition of cationic polyacrylamide:	60 sec.
Addition of silica particles:	75 sec.
Sheet formation:	90 sec.

[0057] The paper sheets were evaluated as in Example 2. The results are shown in Table 2.

Table 1

Test No.	Mode of Addition	Filler	Cobb <sub>60</sub>
1	Separately Added	Untreated PCC + CMC	65



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(continued)

Test No.	Mode of Addition	Filler	Cobb <sub>60</sub>
2	CMC-treated PCC Added	ICP2	35

### Example 4

**[0058]** Products of Example 1 were used and evaluated in papermaking processes. Paper sheets were manufactured from a fibre furnish containing 70% by weight of mixed hardwood pulp and 30% by weight of softwood pulp refined at 22° and 25° SR, respectively, in a method similar to Example 3 except that no cationic starch was used and use was made of untreated SuperFill<sup>®</sup> filler (CP2) or CMC-treated SuperFill<sup>®</sup> filler (ICP3 and IP4), which was added in an amount so as to give a paper sheet containing 30% by weight of SuperFill<sup>®</sup> filler. The addition sequence was as follows:

Addition of SuperFill <sup>®</sup> filler:	0 sec.
Addition of cationic polyacrylamide:	45 sec.
Addition of silica particles:	75 sec.
Addition of AKD:	90 sec.

**[0059]** The results are set forth in Table 3.

Table 3

Test No.	Filler	Cobb <sub>60</sub>
1	CP2	80
2	ICP3	50
3	IP4	21

### Claims

1. A filler comprising calcium salt and cellulose derivative, **characterised in that**

the cellulose derivative is an amphoteric cellulose derivative containing cationic groups and anionic groups, the cellulose derivative has a net anionic substitution, wherein there is a net excess of anionic groups and a degree of anionic substitution ( $DS_A$ ) of from 0.01 to 1.0, and the cellulose derivative has a degree of substitution of net anionic groups ( $DS_{NA}$ ) of from 0.01 to 0.60, wherein the net anionic groups are defined as the average number of anionic groups minus the average number of cationic groups per glucose unit.

2. The filler according to claim 1, **characterised in that** the degree of net anionic substitution ( $DS_{NA}$ ) is at least 0.05.
3. The filler according to claim 1 or 2, **characterised in that** the degree of net anionic substitution ( $DS_{NA}$ ) is from about 0.15 to about 0.40.
4. The filler according to claim 1, 2 or 3, **characterised in that** the cellulose derivative is a cellulose ether.
5. The filler according to any one of the preceding claims, **characterised in that** the cellulose derivative contains carboxymethyl groups.
6. The filler according to any one of the preceding claims, **characterised in that** the cellulose derivative contains quaternary ammonium groups.
7. The filler according to any one of the preceding claims, **characterised in that** the cellulose derivative is at least partly water soluble.

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8. The filler according to any one of the preceding claims, **characterised in that** the filler has a cellulose derivative content from 0.3 to 10 % by weight, based on the weight of the solids of the filler.
- 5 9. The filler according to any one of the preceding claims, **characterised in that** the filler has a calcium salt content from 60 to about 80 % by weight, based on the weight of the solids of the filler.
10. The filler according to any one of the preceding claims, **characterised in that** the calcium salt is calcium carbonate.
- 10 11. The filler according to any one of the preceding claims, **characterised in that** the calcium salt is precipitated calcium carbonate.
12. The filler according to any one of the claims 1 to 10, **characterised in that** the calcium salt is ground calcium carbonate.
- 15 13. The filler according to any one of the preceding claims, **characterised in that** the filler further comprises fibres or fibrils of cellulose or lignocellulose.
14. The filler according to any one of the preceding claims, **characterised in that** the filler is essentially free from fibres or fibrils of cellulose or lignocellulose.
- 20 15. Sized paper comprising a filler according to any one of the claims 1 to 14.
16. The sized paper according to claim 15, **characterised in that** the total filler content of the paper is from 5 to 40 % by weight, based on dry paper.
- 25 17. A process for the production of sized paper which comprises providing an aqueous suspension containing cellulosic fibres, introducing into the suspension a filler according to any one of claims 1 to 14, and dewatering the suspension to form a web or sheet of paper.
- 30 18. The process according to claim 17, **characterised in that** the filler is added in an amount of from 5 to 30 % by weight, based on dry fibre.
19. The process according to claim 17 or 18, **characterised in that** it further comprises adding a cellulose-reactive sizing agent to the suspension.
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### Patentansprüche

- 40 1. Füllstoff umfassend Calciumsalz und Cellulosederivat, **dadurch gekennzeichnet, dass**
- das Cellulosederivat ein amphoterer Cellulosederivat ist, das kationische Gruppen und anionische Gruppen enthält,
- 45 das Cellulosederivat eine anionische Nettosubstitution aufweist, wobei ein Nettoüberschuss anionischer Gruppen und ein anionischer Substitutionsgrad ( $DS_A$ ) von 0,01 bis 1,0 vorliegt und das Cellulosederivat einen Substitutionsgrad anionischer Nettogruppen ( $DS_{NA}$ ) von 0,01 bis 0,60 aufweist, wobei die anionischen Nettogruppen als durchschnittliche Anzahl anionischer Gruppen minus der durchschnittlichen Anzahl kationischer Gruppen pro Glucoseinheit definiert sind.
- 50 2. Füllstoff nach Anspruch 1, **dadurch gekennzeichnet, dass** der Grad der Nettoanionensubstitution ( $DS_{NA}$ ) mindestens 0,05 beträgt.
3. Füllstoff nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** der Grad der Nettoanionensubstitution ( $DS_{NA}$ ) etwa 0,15 bis etwa 0,40 beträgt.
- 55 4. Füllstoff nach Anspruch 1, 2 oder 3, **dadurch gekennzeichnet, dass** das Cellulosederivat ein Celluloseether ist.
5. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Cellulosederivat Car-

boxymethylgruppen enthält.

- 5
6. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Cellulosederivat quartäre Ammoniumgruppen enthält.
7. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Cellulosederivat mindestens teilweise wasserlöslich ist.
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8. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Füllstoff einen Cellulosederivatgehalt von 0,3 bis 10 Gew.-%, auf das Gewicht der Feststoffe des Füllstoffs bezogen, aufweist.
9. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Füllstoff einen Calciumsalzgehalt von 60 bis etwa 80 Gew.-%, auf das Gewicht der Feststoffe des Füllstoffs bezogen, aufweist.
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10. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Calciumsalz Calciumcarbonat ist.
11. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Calciumsalz ausgefälltes Calciumcarbonat ist.
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12. Füllstoff nach einem der Ansprüche 1 bis 10, **dadurch gekennzeichnet, dass** das Calciumsalz gemahlenes Calciumcarbonat ist.
13. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Füllstoff ferner Fasern oder Fibrillen aus Cellulose oder Lignocellulose umfasst.
- 25
14. Füllstoff nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** der Füllstoff im Wesentlichen frei von Fasern oder Fibrillen aus Cellulose oder Lignocellulose ist.
- 30
15. Geleimtes Papier, umfassend einen Füllstoff nach einem der Ansprüche 1 bis 14.
16. Geleimtes Papier nach Anspruch 15, **dadurch gekennzeichnet, dass** der gesamte Füllstoffgehalt des Papiers 5 bis 40 Gew.-%, auf trockenes Papier bezogen, beträgt.
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17. Verfahren zur Herstellung von gelemtem Papier, das das Bereitstellen einer wässrigen Suspension, die Cellulosefasern enthält, das Einbringen eines Füllstoffs nach einem der Ansprüche 1 bis 14 in die Suspension und das Entwässern der Suspension zur Bildung einer Bahn oder eines Blatts aus Papier umfasst.
18. Verfahren nach Anspruch 17, **dadurch gekennzeichnet, dass** der Füllstoff in einer Menge von 5 bis 30 Gew.-%, auf trockene Faser bezogen, zugesetzt wird.
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19. Verfahren nach Anspruch 17 oder 18, **dadurch gekennzeichnet, dass** es ferner das Zusetzen eines celluloseaktiven Leimungsmittels zu der Suspension umfasst.

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## Revendications

1. Charge comprenant un sel de calcium et un dérivé de cellulose, **caractérisée en ce que**

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le dérivé de cellulose est un dérivé de cellulose amphotère contenant des groupes cationiques et des groupes anioniques,

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le dérivé de cellulose a une substitution anionique nette, dans laquelle, il y a un excès net de groupes anioniques et un degré de substitution anionique ( $DS_A$ ) allant de 0,01 à 1,0, et le dérivé de cellulose a un degré de substitution de groupes anioniques nets ( $DS_{NA}$ ) allant de 0,01 à 0,60, dans laquelle les groupes anioniques nets sont définis comme le nombre moyen de groupes anioniques moins le nombre moyen de groupes cationiques par motif de glucose.

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2. Charge selon la revendication 1, **caractérisée en ce que** le degré de substitution anionique nette ( $DS_{NA}$ ) est d'au moins 0,05.
- 5 3. Charge selon la revendication 1 ou 2, **caractérisée en ce que** le degré de substitution anionique nette ( $DS_{NA}$ ) est d'environ 0,15 à environ 0,40.
4. Charge selon la revendication 1, 2 ou 3, **caractérisée en ce que** le dérivé de cellulose est un éther de cellulose.
- 10 5. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** le dérivé de cellulose contient des groupes carboxyméthyle.
6. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** le dérivé de cellulose contient des groupes ammonium quaternaire.
- 15 7. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** le dérivé de cellulose est au moins partiellement soluble dans l'eau.
8. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** la charge a une teneur en dérivé de cellulose de 0,3 à 10 % en poids, sur la base du poids des matières solides de la charge.
- 20 9. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** la charge a une teneur en sel de calcium de 60 à environ 80 % en poids, sur la base du poids des matières solides de la charge.
- 25 10. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** le sel de calcium est du carbonate de calcium.
11. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** le sel de calcium est du carbonate de calcium précipité.
- 30 12. Charge selon l'une quelconque des revendications 1 à 10, **caractérisée en ce que** le sel de calcium est du carbonate de calcium broyé.
13. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** la charge comprend en outre des fibres ou des fibrilles de cellulose ou de lignocellulose.
- 35 14. Charge selon l'une quelconque des revendications précédentes, **caractérisée en ce que** la charge est essentiellement exempte de fibres ou de fibrilles de cellulose ou de lignocellulose.
- 40 15. Papier collé comprenant une charge selon l'une quelconque des revendications 1 à 14.
16. Papier collé selon la revendication 15, **caractérisé en ce que** la teneur totale en charge du papier est de 5 à 40 % en poids, sur la base du papier sec.
- 45 17. Procédé de production de papier collé qui comprend la fourniture d'une suspension aqueuse contenant des fibres cellulosiques, l'introduction dans la suspension d'une charge selon l'une quelconque des revendications 1 à 14, et la déshydratation de la suspension pour former une bande ou une feuille de papier.
18. Procédé selon la revendication 17, **caractérisé en ce que** la charge est ajoutée en une quantité de 5 à 30 % en poids, sur la base de la fibre sèche.
- 50 19. Procédé selon la revendication 17 ou 18, **caractérisé en ce qu'il** comprend en outre l'ajout d'un agent d'encollage réactif à la cellulose à la suspension.

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**REFERENCES CITED IN THE DESCRIPTION**

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