



(51) International Patent Classification:

**D21H 17/25** (2006.01)    **D21H 17/42** (2006.01)  
**D21H 17/28** (2006.01)    **D21H 17/63** (2006.01)  
**D21H 17/29** (2006.01)    **D21H 17/67** (2006.01)  
**D21H 17/34** (2006.01)    **D21H 17/68** (2006.01)  
**D21H 17/41** (2006.01)    **D21H 17/00** (2006.01)

(21) International Application Number:

PCT/US2013/063310

(22) International Filing Date:

3 October 2013 (03.10.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/710,624    5 October 2012 (05.10.2012)    US  
61/718,137    24 October 2012 (24.10.2012)    US  
61/857,600    23 July 2013 (23.07.2013)    US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CL, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

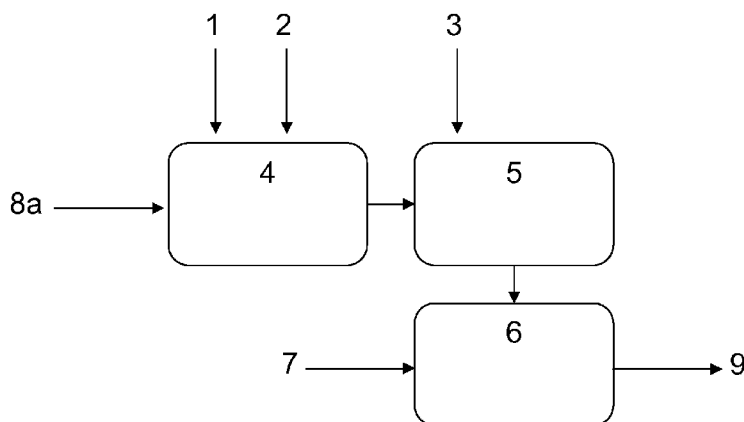
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: FILLER SUSPENSION AND ITS USE IN THE MANUFACTURE OF PAPER

FIG.1



(57) Abstract: Provided herein are filler suspensions comprising an ionic starch, a complementary ionic coadditive and filler particles. Pulp furnishes comprising the filler suspensions and paper comprising the pulp furnish are also provided. Processes for making the filler suspensions and processes for their use in manufacturing paper are also provided.

WO 2014/055787 A1

## FILLER SUSPENSION AND ITS USE IN THE MANUFACTURE OF PAPER

### FIELD

[0001] The invention herein relates to a filler suspension comprising filler particles, an ionic starch and a complementary ionic coadditive. Methods of use of the suspension for the preparation of a paper furnish and the manufacture of a paper from the furnish are also provided.

### BACKGROUND

[0002] In the manufacture of filled papers, filler slurry is conventionally added to a pulp suspension before it is transferred to the forming section of a paper-making machine. A retention aid or retention aid system comprising several components is generally added to the pulp/filler suspension to form what is referred to in the paper-making art as the "furnish" to retain the filler in the resulting paper sheet.

[0003] Adding filler to paper can provide numerous improvements in sheet properties, including improved opacity, brightness, feel, and print definition. Further, when the filler is cheaper than the pulp, addition of filler to the sheet results in cost savings. These savings can be substantial when low cost fillers, such as precipitated calcium carbonate (PCC), are used to replace expensive chemical pulp fibers. Moreover, filled paper can be easier to dry than paper with no filler and, as a result, a paper machine can run faster with less steam consumption, which can further reduce costs and improve productivity.

[0004] For a given sheet weight, however, there are limits to the amount of filler that can be added. The strength of the resulting paper is a prime factor, together with paper machine efficiency that limits filler content, although other factors such as retention, drainage and sizing are also a consideration.

[0005] Making paper with high filler content requires an efficient retention aid system. The retention aid should provide good filler retention under the high shear and turbulence occurring in the paper manufacturing process and should improve drainage without impairing formation. The retention aid chemicals are generally added to the furnish prior to or at the inlet to the headbox of the paper machine. The retention aids are typically one, two or three component chemical additives that

improve filler and fines retention by a bridging and/or flocculation mechanism. The chemicals help attach the filler particles and fines (small fibrous fragments) to the long fibers or cause their aggregation into larger flocculated particles which are more easily retained in the web. In order to create the attachment and flocculation, the chemicals must adsorb on the surfaces of the fillers, fines and fibers. The degree of adsorption of chemicals and the attachment forces are influenced by many things including furnish cleanliness and furnish chemistry, the properties of the added chemicals, the degree of shear in the papermaking process and the contact time between the retention aids and the furnish components.

[0006] An on-going industry trend is to increase filler content in paper to further reduce cost. Paper strength, however, is reduced by replacement of fiber with filler, not only because there are fewer fibers in the sheet, which reduces the number of fiber-fiber bonds, but also because the presence of the filler reduces contact between the remaining fibers. Filler particles do not bond among themselves and their location at the fiber-fiber bonded area prevents hydrogen bonding from occurring between the pulp fibers. As a result, high amounts of filler produces a weaker sheet that can break more easily on the paper machine, size press, coater, winders and printing press. Weaker fiber-fiber bonding also decreases the surface strength of the paper, causing a reduction in pick resistance and an increase in linting. Poor bonding of filler particles in the fibrous structure can also increase dusting in the pressroom.

[0007] In general, all inorganic fillers generally used in paper making such as, without limitation, clay, ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), chalk, talc, titanium dioxide, ground calcium sulphate (GCS) and precipitated calcium sulphate (PCS) are known to impair paper strength and increase demand for chemicals. Fillers with high surface areas have substantial negative effects on strength and increase the chemical demand for additives used for strength, sizing and retention. Due to its shape and narrow particle size distribution PCC has a tendency to reduce bonding in a sheet more than other common papermaking fillers, such as chalk, GCC and clay, and also gives the sheet an open structure which makes the sheet permeable or porous. As the filler content is increased in the furnish the demand for sizing chemicals, such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA), is increased to maintain the

desired degree of sizing/ water repellence. This is because a disproportionate fraction of the sizing chemical is adsorbed on the filler particles. In recent years many paper mills making wood-containing paper grades have converted to neutral papermaking to allow use of bright calcium carbonate fillers, such as GCC and PCC. Major concerns with the use of calcium carbonate in these grades of paper remain, however, particularly in the areas of retention, sheet strength and printing operations.

[0008] Another ongoing industry trend is to decrease sheet grammage to reduce costs. Unfortunately, as the grammage is decreased, nearly all paper properties deteriorate including the limiting factors of opacity, bending stiffness and permeability. Reduction in grammage may also decrease retention of filler during the papermaking process and increase the frequency of sheet breaks both on the paper machine and during converting and printing. To overcome the loss in sheet opacity the papermaker can add more high opacity filler, but this can cause further deterioration in sheet strength. The industry needs cost-efficient technology for the production of lightweight grades of paper with good filler retention and drainage and acceptable strength, formation, optical, and printing properties.

### **SUMMARY**

[0009] Thus, an aspect of this invention is a filler suspension for use in papermaking, comprising filler particles, ionic starch and a complementary ionic coadditive.

[0010] In an aspect of this invention, the filler particles are selected from the group consisting of clay, talc, synthetic silicates, sodium magnesium alumino silicate, sodium alumino silicate, ground calcium carbonate (GCC), chalk, precipitated calcium carbonate (PCC), ground calcium sulphate (GCS), precipitated calcium sulphate (PCS), titanium dioxide and combinations thereof.

[0011] In an aspect of this invention, the ionic starch is raw starch.

[0012] In an aspect of this invention, the ionic starch is swollen ionic starch.

[0013] In an aspect of this invention, the ionic starch is cooked ionic starch.

[0014] In an aspect of this invention, the ionic starch is cationic.

[0015] In an aspect of this invention, the ionic starch is anionic.

[0016] In an aspect of this invention, the ionic starch is amphoteric.

[0017] In an aspect of this invention, the ionic starch is selected from the group consisting of corn starch, rice starch, potato starch, cassava starch, tapioca starch, waxy corn starch, wheat starch, sorghum starch and waxy sorghum starch.

[0018] In an aspect of this invention, the swollen ionic starch is formed by heating an aqueous suspension of raw starch at a gel point temperature of the raw starch  $\pm 10$  °C.

[0019] In an aspect of this invention, the swollen ionic starch is formed by heating an aqueous suspension of raw starch in a temperature range from the gel point temperature of the starch to the gel point temperature of the starch plus 10 °C.

[0020] In an aspect of this invention, the complementary ionic coadditive is an anionic flocculant.

[0021] In an aspect of this invention, the anionic flocculants comprise copolymers of acrylamide and sodium acrylate.

[0022] In an aspect of this invention, the complementary ionic coadditive is selected from the group consisting of NALCO 61815, Nalco 61816, Nalco 61830, Fennosil® ES210, Fennosil® ES211, Telioform® M305.

[0023] In an aspect of this invention, the complementary ionic coadditive is an anionic inorganic microparticle.

[0024] In an aspect of this invention, the anionic inorganic particles are selected from the group consisting of bentonites, colloidal silicas, sodium borosilicates, aluminium hydroxides or combinations thereof.

[0025] In an aspect of this invention, the complementary ionic coadditive is nanocellulose.

[0026] In an aspect of this invention, the complementary ionic coadditive is polyvinyl alcohol.

[0027] In an aspect of this invention, the complementary ionic coadditive is anionic or amphoteric PVAm.

[0028] In an aspect of this invention, the complementary coadditive is a biopolymer.

[0029] In an aspect of this invention, the biopolymer is starch-based.

[0030] In an aspect of this invention, the starch-based biopolymer is EcoSphere® 2202 binder.

[0031] In an aspect of this invention, the complementary ionic coadditive is anionic polyacrylic acid or sodium salt of polyacrylic acid.

[0032] In an aspect of this invention, the complementary ionic coadditive is a natural polymer.

[0033] In an aspect of this invention, the natural polymer is selected from the group consisting carboxymethylcellulose, natural gums, soy polymers or combinations thereof.

[0034] In an aspect of this invention, the filler particles are precipitated calcium carbonate.

[0035] An aspect of this invention is a pulp furnish comprising pulp fiber and a filler suspension of this invention.

[0036] In an aspect of this invention, the above pulp furnish further comprises an additive selected from the group consisting of a sizing agent, a dry strength agent, a wet strength agent, a retention aid and other functional chemicals such as an optical brightening agent, a dye, a defoamer, a bioside and combinations thereof.

[0037] An aspect of this invention is a paper product comprising the above pulp furnish.

## DETAILED DESCRIPTION

### BRIEF DESCRIPTION OF THE FIGURES

[0038] **FIG. 1** is a schematic of a paper-making process wherein an ionic starch, a complementary ionic coadditive and filler particles are added to an aqueous medium essentially simultaneously.

[0039] **FIG. 2** is a schematic of a paper-making process wherein a complementary ionic coadditive is premixed with an ionic starch in an aqueous medium before addition of the filler particles.

[0040] **FIG. 3** is a schematic of a paper-making process wherein a complementary ionic coadditive is premixed with filler particles in an aqueous medium before addition of an ionic starch starch.

[0041] **FIG. 4** is a schematic of a paper-making process wherein an ionic starch is premixed with filler particles in an aqueous medium before addition of a complementary ionic coadditive.

[0042] **FIG. 5** is a graph of the viscosity response of potato starch when heated to and beyond its gel temperature.

[0043] **FIG. 6** comprises microscopic images of potato starch granules as they are heated in water at various temperatures.

[0044] **FIG. 7** is a graph showing the tensile strength of a paper sheet made using various filler compositions including those of this invention.

[0045] **FIG. 8** is a graph showing the stiffness of a paper sheet made using various filler compositions including those of this invention.

#### **BRIEF DESCRIPTION OF THE TABLES**

[0046] **Table 1** shows a comparison of paper sheet properties in papers made using filler compositions comprising swollen cationic starch and swollen cationic starch plus anionic micropolymer co-additives.

[0047] **Table 2** shows a comparison of paper sheet properties in papers made using filler compositions in which the components of the composition were added in different addition orders.

[0048] **Table 3** shows a comparison of the tensile strength improvements of papers made with PCC filler treated with swollen cationic starch only and with PCC filler treated with swollen cationic starch and a co-additive.

[0049] **Table 4** shows a comparison of percent paper tensile index/breaking length improvement depending on the addition order of swollen starch and various co-additives to PCC.

[0050] **Table 5** shows a comparison of tensile strength improvements over a no-PCC treatment baseline in papers as the result of various PCC treatments.

[0051] **Table 6** shows a comparison of paper properties using a filler composition comprising PCC treated with swollen cationic starch or cooked cationic starch or cooked cationic starch with various co-additives.

#### **Discussion**

[0052] Use of the singular herein includes the plural and *vice versa* unless expressly stated to be otherwise. That is, "a" and "the" refer to one or more of whatever the word modifies. For example, "a lightly cross-linked polymer" includes one such polymer, two such polymers or, under the right circumstances, an even greater number of such polymers. By the same token, words such as, without limitation, "sizing agents" may refer to a plurality of such agents or simply to one

such agent, unless, again, it is expressly stated or obvious from the context that such is not intended.

[0053] Words of approximation such as, without limitation, "about," "substantially," "essentially" and "approximately" mean that the feature so modified need not be exactly that which is expressly described but may vary from that written description to some extent. The extent to which the description may vary will depend on how great a change can be instituted and have one of ordinary skill in the art recognize the modified feature as still having the required characteristics and capabilities of the unmodified feature. In general, but subject to the preceding discussion, an expressly stated or implied value herein that is modified by a word of approximation may vary from the stated value by  $\pm 15\%$ .

### **Compositions**

[0054] In one embodiment herein there is provided a filler suspension for use in papermaking, comprising filler particles, an ionic starch and a complementary ionic co-additive in a liquid vehicle, typically water.

[0055] In another embodiment, there is provided a pulp furnish comprising, in an aqueous vehicle, a filler suspension as set forth herein and pulp fibers. The furnish may also contain other papermaking agents.

[0056] In still another embodiment, there is provided a method of producing paper by adding a filler suspension of this invention to a pulp fiber stock to form a pulp furnish, and then manufacturing paper from the furnish. Other anionic and cationic agents can be added to the furnish to enhance retention and improve drainage. As noted previously, the furnish may also contain other papermaking agents as such are known to those skilled in the art.

[0057] The invention also provides processes for producing starch/coadditive compositions and their combination with filler particles to form a filler suspension.

[0058] The starch herein may be raw, swollen, cooked or combinations thereof.

[0059] As used herein, "raw" starch refers to starch that has not been subjected to treatment with hot water or steam sufficient to render it swollen or cooked as these states are described below.



[0060] As used herein, a “swollen” starch refers to raw starch granules that have absorbed water and have expanded, preferably at present to a state in which no further water can be absorbed without rupturing the swollen granules. Exemplary swollen starches suitable for use in a filler suspension herein include, but are not limited to, those disclosed in U.S. Patent Nos. 7,074,845; 7,625,962; and 8,354,004, each of which is incorporated by reference as if set forth in its entirety herein.

[0061] In general, preparation of a swollen starch requires that the swelling be performed under carefully controlled conditions of temperature and time. The other parameters of interest include slurry pH, consistency and mixing. Control parameters will differ from starch type to starch type and are usually determined empirically for each type of starch before being used in mill-scale paper production. The general procedure is to suspend raw ionic starch in cold water and then heat the suspension until the starch is swollen. The swollen starch is then mixed with a complementary ionic coadditive and filler particles in any desired order, that is, all components may be added essentially simultaneously or any two of the components can be premixed and the remaining component added thereafter, to form a filler suspension. For example, in FIG. 1, swollen ionic starch 1, complementary ionic coadditive 8a and filler particles 2 are mixed together in mixer 4 to form a filler suspension which is then transferred to mixer 5, where it is mixed with pulp fiber 3 to form a furnish. In FIG. 2, swollen ionic starch 1 and complementary ionic coadditive 8a are premixed and this combination is subsequently mixed with filler particles 2 in mixer 4 after which the formed filler suspension is mixed with pulp fiber 3 in mixer 5. In FIG. 3, complementary ionic coadditive 8a is premixed with filler particles 2 and that combination is mixed with ionic starch 1 in mixer 4 and the formed filler suspension is transferred to mixer 5 where it is mixed with pulp fiber 3 to form a furnish. In FIG. 4, ionic starch 1 and filler particles 2 are premixed in mixer 4 and the premix is transferred to mixer 5, complementary ionic coadditive 8a being added to the premix essentially in transit between mixer 4 and mixer 5. In each of these situations, the furnish comprising the filler suspension is subsequently transferred to paper machine 6 along with optional additives 7 to form paper 9. During the paper drying operation, retained swollen starch granules will rupture, liberating amylopectin and amylose macromolecules, which operate to bond the solid components of the sheet.

[0062] As used herein “cooked” starch refers to starch that has been heated to a temperature above its gel point and held there until the starch granules have swollen and essentially all the swollen granules have ruptured.

[0063] The combination of ionic starch, ionic coadditive and filler particles can be used for papermaking under acid, neutral or alkaline conditions. The compositions are used primarily to assure that the filler and starch are well-retained in paper sheets during the paper-making process while having a minimal negative effect on sheet strength. Using ionic starch/ionic coadditive/filler particle compositions tends to result in greater strength than using starch or coadditive alone with the filler particles.

### **Fillers**

[0064] The filler particles can be any known to those of skill in the art and the filler suspension can comprise a single filler or more than one filler. The fillers particles are typically inorganic materials having an average particle size ranging from 0.5 to 30  $\mu\text{m}$ , more usually 1 to 10  $\mu\text{m}$ , such as, without limitation, clay, ground calcium carbonate (GCC), chalk, precipitated calcium carbonate (PCC), talc, ground calcium sulphate (GCS) and precipitated calcium sulphate (PCS), titanium dioxide, synthetic silicates, sodium magnesium alumino silicate, sodium alumino silicate and blends thereof. The pulp slurry to which the filler suspension is added can be composed of mechanical pulp, chemical pulp, recycled pulp and mixtures thereof.

### **Starch**

[0065] Starches suitable for use in this invention include, without limitation, those originating from corn, waxy corn, potato, wheat, tapioca, sorghum, waxy sorghum and rice. The starch may be cationic, anionic or amphoteric; each of these forms is well-known in the art and generally commercially available. By way of non-limiting example, starches can be rendered cationic by inclusion of quaternary ammonium cations in the starch, anionic by include carboxyl or sulfonic groups in the starch and amphoteric by preparing a starch that includes a combination of the foregoing. Since all these ionic starch forms are well-known to those skilled in the paper-making art, they are not further described herein.

[0066] Starch granules are insoluble in cold water. To disperse or “cook” a starch, the starch is heated in aqueous suspension. As heating proceeds, the starch

granules first go through a stage of slight, reversible swelling until a critical temperature, referred to as the “pasting,” “gelatinization” or simply “gel” temperature, is reached where massive swelling occurs, which causes a large increase in viscosity. If held for a sufficient period above the gel temperature, the viscosity reverts to lower levels due to the rupture of the swollen granules. Each variety of starch has its own gel temperature. The gel temperature for many starches is available in extant literature or it can be readily empirically determined by heating a given starch suspension while monitoring viscosity. Swollen starch granules are distinct from cooked starch. Cooked starch results when swollen starch granules rupture at temperatures above the gel temperature and thereby release amylose and amylopectin, which dissolve in the aqueous medium.

[0067] By carefully controlling the treatment of a particular starch, it may be rendered swollen or cooked. With regard to swollen starch, depending on the starch source, the ultimate particle size of the swollen starch granules ranges from about 25  $\mu\text{m}$  to about 100  $\mu\text{m}$ . A representative, but non-limiting, example of a swollen starch preparation is shown in the Examples.

### **Coadditive**

[0068] The coadditive is included in the filler suspension to improve the effect of the ionic starch in enhancing the properties of a filled paper by modification of the filler suspension. The coadditive may be cationic, anionic or amphoteric. It is selected so as to have a net charge that is complementary to the net charge on the ionic starch. By “complementary” is meant that, if the starch is cationic, it is presently preferred that the coadditive be anionic and *vice versa*. If the starch is amphoteric, the coadditive may be cationic, anionic or itself amphoteric. Anionic coadditives include, without limitation, carboxymethylcellulose, nanocellulose, polyacrylic acid, alginate, colloidal silica, bentonite, polyacrylamide, a natural gum and a soluble soap. Cationic coadditives include, without limitation, polyethyleneimine, chitosan, polyvinylamine, poly(dadmac), polyacrylamide, alum, trivalent and tetravalent cations. Soy polymer may also be used as a coadditive. More than one coadditive may be used with a particular starch and filler.

[0069] A non-limiting example of an amphoteric coadditive which is suitable as a coadditive for use in a filler suspension of this invention is Ashland-Hercules Hercobond<sup>®</sup> 1303.

[0070] Other materials suitable for use as a coadditive in a filler suspension of this invention are anionic colloidal silica nanoparticles such as, without limitation, Eka NP<sup>®</sup> 090, Eka NP<sup>®</sup> 200, Eka NP<sup>®</sup> 320, Eka NP<sup>®</sup> 32K, Eka NP<sup>®</sup> 442, Eka NP<sup>®</sup> 590/670, Eka NP<sup>®</sup> 780, Eka NP<sup>®</sup> 882, Eka NP<sup>®</sup> 890 and EKA NP<sup>®</sup> 2180, all from AkzoNobel; Fennosil<sup>®</sup> 525 from Kemira, and POSITEK<sup>®</sup> 8699 from Nalco.

[0071] Also suitable for use as a coadditive in a filler suspension of this invention are Nalco Ultra POSITEK<sup>®</sup> 8692, 8693, BD420 and TR420, which are sodium borosilicate nanoparticles (typically 1 to 100 nm in size).

[0072] Altonite<sup>®</sup> from S&B Industrial Minerals, Fennolite<sup>®</sup> LF5 from Kemira and Hydrocol<sup>®</sup> from BASF are bentonites that are suitable for use as coadditives in a filler suspension of this invention.

[0073] Anionic aluminum hydroxide microparticles are also deemed suitable for use as a coadditive in filler suspensions of this invention.

[0074] Perform SP<sup>®</sup> 7200 and 9232, which are anionic acrylamide copolymer from Hercules Incorporated (now Ashland-Hercules), are also suitable for use as a coadditive in a filler suspension of this invention. Perform<sup>®</sup> 7200 is described in MSDS 999 1060 1076, Ver. 3, issued 12 February 2007.

[0075] Telioform<sup>®</sup> M305, a copolymer of sodium acrylate and acrylamide dispersed in mineral oil, as described in an MSDS issued 23 March 2006, from Ciba Specialty Chemicals Corporation (now BASF), is likewise suitable as a coadditive for use in a filler suspension of this invention. Other Telioform<sup>®</sup> compositions such as, without limitation, Telioform<sup>®</sup> M100, M135, M200, M300, S10, M100A, M8A and SC22, may also be suitable for use as a coadditive in a filler suspension of this invention.

[0076] The Fennosil<sup>®</sup> family of additives including the anionic forms exemplified by Fennosil<sup>®</sup> ES-210, Fennosil<sup>®</sup> ES-211 (both based on acrylamide/acrylic acid copolymers) and Fennosil<sup>®</sup> ES-325; as well as the cationic forms exemplified by Fennosil<sup>®</sup> E130 (formulation comprising acrylamide/p-amine), E128 (formulation comprising polyacrylamide/polydimethyldiallylammonium chloride (DADMAC) copolymer), ES-325 (a formulation comprising polyacrylamide/salt) and

E-126 (acrylamide/p-amine) are also suitable as coadditives in a filler suspension of this invention.

[0077] Nanocellulose such as without limitation described in WO 2007/091942 and WO 2009/126106, both of which are incorporated by reference in their entirety herein, may also be suitable as coadditives for use in a filler suspension of this invention.

[0078] Still other materials presently deemed suitable for use as coadditives in filler suspensions of this invention are cellulose-based materials and derivatives such as Engineered Cellulose Additive (ECA) from AkzoNobel; noil fibrils as described in U.S. Patent No. 6,156,118, which is incorporated by reference as if fully set forth herein; hemicellulose and high hemicellulose-containing materials.

[0079] Carboxymethylcellulose (CMC) is also suitable as a coadditive in a filler suspension of this invention.

[0080] Natural gums, such as guar and xanthan are also suitable coadditives in filler suspensions of this invention.

[0081] Other materials deemed at present to be suitable coadditives for use in the filler suspension of this invention are NALCO 64110, 64114 and, 64170, which are glyoxylated DADMAC/acrylamide copolymer compositions and NALCO 61815, 61816 and 61830, which are anionic flocculants that are copolymers of acrylamide and sodium acrylate as described generally in U.S. Patent 8,088, 213, which is incorporated by reference as if fully set forth herein.

[0082] Still other materials suitable for use as coadditives in filler suspensions of this invention are Ashland-Hercules Hercobond<sup>®</sup> HA5305 and SP7200 and Eka PL8660.

[0083] Polyvinyl alcohol (PVA) is likewise suitable for use as a coadditive in filler suspensions of this invention.

[0084] Also suitable as coadditives in filler suspensions of this invention are anionic polyvinylamines (PVAm) and amphoteric polyvinylamines such as, without limitation, the amphoteric terpolymer of vinylformamide, vinylamine and acrylic acid, a non-limiting example of which is XELOREX<sup>®</sup> F3000 from BASF.

[0085] Biopolymers may also be used as coadditives in filler suspensions of this invention. Suitable biopolymers for use as filler additives include, without limitation, starch-based biopolymers. The biopolymer may be micro- or nano-

particulate. Biopolymers include, without limitation, EcoSphere<sup>®</sup> 2202 binder from Ecosynthetix of Burlington, Ontario, Canada.

[0086] If the coadditive is a polymer, it may be not cross-linked, lightly cross-linked or heavily cross-linked.

[0087] The coadditive may be water-soluble or water-insoluble. A non-limiting example of a water-soluble coadditive is Teliiform<sup>®</sup> M303, a polyacrylamide-based anionic polymer.

[0088] A polymeric coadditive may be a micropolymer. As used herein, a "micropolymer" refers to the polymeric particles obtained by emulsion polymerization, dispersion polymerization and water-in-water polymerization wherein the reaction of water-soluble monomers is carried out in the presence of coagulants such as, without limitation, polyamines such as DADMAC or DIMAPA. The micropolymer may be "structured," that is, the individual polymer strands within the polymeric particles may adopt a stable three-dimensional structure.

[0089] By "lightly cross-linked" is meant that the cross-linked polymer remains substantially water soluble. That is, a lightly cross-linked polymer appears more like a "branched" polymer than a fully cross-linked polymer in which the polymer chains are inextricably intertwined and is thereby rendered insoluble in water. As used herein, lightly cross-linked and branched are used interchangeably to refer to a polymer that is cross-linked but is still water-soluble. Examples of anionic, branched, water-soluble polymers are described in U.S. Patent Nos. 5,958,188, 6,391,156 B1, 6,395,134 B1, 6,406,593 B1 and 6,454,902 B1, which are hereby incorporated by reference in their entireties as if fully set forth herein.

[0090] "Heavily cross-linked" simply refers to a polymer that, while soluble when not cross-linked or lightly cross-linked, is no longer water soluble as the result of the degree of cross-linking.

#### **Filler/ionic starch/ionic coadditive suspension**

[0091] In general, the suspension will comprise 60 to 99.5% by weight filler, 35 to 0.499 % by weight ionic starch and 5.0 to 0.001% by weight complementary ionic coadditive to a total of 100% based on the total solids content of filler particles, ionic starch and complementary ionic coadditive.

[0092] It is understood that the suspension will contain complexes of ionic starch and complementary ionic coadditive but may also contain free ionic starch and free ionic coadditive.

### **Papermaking Agents**

[0093] The compositions, suspensions and furnishes herein may additionally include conventional papermaking agents such as, without limitation, sizing agents such as alkylketene dimer, alkenyl succinic anhydride and rosin; wet and dry strength agents, and cationic or anionic polymeric retention aids. The composition may include a retention aid which may be a single chemical, such as an anionic micro-particle (colloidal silicic acid, bentonite), anionic polyacrylamide, a cationic polymer (cationic polyacrylamide, cationic starch), dual chemical systems (cationic polymer/anionic micro-particle, cationic polymer/anionic polymer) or three component systems (cationic polymer/anionic microparticle/anionic polymer, cationic polymer/anionic micro-polymer/anionic polymer). The choice of retention aid chemicals and their addition points in the paper-forming process will depend on the nature of the ionic charge of the treated filler slurry, the papermaking furnish and the shear forces that occur in paper making process.

[0094] In general, the filler suspension herein is used in an amount of 5% to 70%, as dry solids, based on the dry weight of pulp in the furnish.

[0095] Paper sheets made with filler suspension according to this invention can exhibit greater internal bond strength, as measured by the Scott bond technique, than a control sheet made with no filler treatment. At equal filler content, the wet and dry strength properties of sheets made using the filler suspension herein can be greater than those sheets made with the filler alone.

[0096] The use of a filler suspension of this invention permits the production of filled papers, such as coated and uncoated fine papers, super-calendered papers, and newsprint, with minimal strength loss and good optical properties. Using the filler suspension of this invention can thus allow papermakers to produce filled papers with higher filler content in the paper sheet. In general, the potential benefits from the use of the treated filler suspensions of the present invention include improved sizing, wet strength, dry strength and printability, and/or reduced use of expensive reinforcement chemical pulp fiber.

[0097] Under certain conditions the combination of ionic starch and ionic coadditive may be used to strengthen paper grades that contain no filler such as sack papers and paperboard products.

## **EXAMPLES**

[0098] The examples provided below are intended solely as an aid in understanding various aspects of this invention. They are not intended nor are they to be construed as limiting the scope of this invention in any manner whatsoever.

### **General**

[0099] In the examples that follow, the results were obtained using laboratory scale techniques.

[0100] If the starch to be used is raw, it can be suspended in water or it may be suspended in water and heated to a temperature that is sufficiently below its gel point so as to neither swell the starch to a significant extent nor cook it.

[0101] If, on the other hand, a swollen starch is desired, raw starch, in an aqueous slurry at typically 0.5-20% solids at room temperature may be swollen at temperatures approximately the starch gel point in a batch cooker, a jet cooker or by mixing with hot water. The preferred method is to swell the granules by mixing the starch slurry prepared in cold water with hot water. The temperature of hot water used depends on the consistency of the initial starch slurry in cold water, the final target temperature of the swollen starch, the temperature of the cold starch slurry, pH, and residence time. The temperature and reaction time for preparing the swollen starch depends on the type of starch used, the pH of the starch slurry and heating time. The following are examples of processes for the preparation of swollen starch for the purposes of this invention.

### **Example 1**

[0102] A raw ionic starch dispersion in cold water is swelled by heating it to a temperature that is approximately the gel point of the particular starch. When the starch is swollen, complementary coadditive is added and the mixture is added to an agitated filler suspension.

### **Example 2**

[0103] A starch dispersion is first swelled, then added to an agitated filler suspension followed by the introduction of coadditive. In this method, the starch



powder is dispersed in cold water then mixed with hot water or heated to a temperature that is approximately the starch gel point. The swollen starch is then rapidly mixed with the filler suspension at a temperature below the starch gel point followed by addition of coadditive.

### **Example 3**

[0104] A starch dispersion is first swelled and then added to an agitated coadditive/filler suspension. In this method, the starch powder is dispersed in cold water and then mixed with hot water or heated to a temperature of approximately the gel temperature of the particular starch. The swollen starch is then rapidly mixed with the filler suspension.

[0105] The combination of swollen starch, coadditive and filler is performed under good mixing conditions. Other additives can be added during the preparation of starch/coadditive/filler suspension to form a complex with filler prior to the addition of swollen starch and coadditive.

[0106] The treated filler suspensions can be introduced directly into the pulp slurry or, if desired, can be diluted and added to the paper machine pulp stock prior to the sheet forming process, e.g., at the blend chest, the machine chest, or at the inlet of the fan pump. In general, the treated-filler suspensions tend to retain their flocculation characteristics over time when added to papermaking pulp slurries. To enhance filler retention the dosing of retention aids such as anionic micro-particles (colloidal silica, bentonite, organic micropolymers), anionic polymers (anionic polyacrylamide), cationic polymers (cationic polyacrylamide, cationic starch) can be increased.

#### Example 4

[0107] A 0.3 % concentration stock was prepared by mixing internal cationic starch with pulp furnish followed by pretreated PCC and finally retention aid. 80 g/m<sup>2</sup> wood-free handsheets were made using a dynamic sheet former (DSF) followed by dynamic sheet pressing and drying at 120 °C. Prior to paper testing the paper sheets were colandered under the same conditions and then conditioned at 50% relative humidity (RH) and 22 °C.

[0108] The raw materials used in the sheet making were the following:  
Fiber: 100 % eucalyptus used as pulp, refined to SR 30 (at 20 °C) using a Valley Beater lab refiner.

[0109] Filler: precipitated calcium carbonate (ALBACAR<sup>®</sup> LO PCC) from Specialty Minerals Inc., average particle size 2.3 µm. The PCC content in the sheets varied between 19.3 % and 25.9 % by weight.

[0110] Swollen cationic starch used for PCC pretreatment: Cationic potato starch. Swollen cationic starch was prepared by mixing dry cationic starch powder with water to make 3 % solids slurry, which was then heated to 63 °C under mixing. Swollen cationic starch was used for PCC pretreatment by mixing 5 kg swollen cationic starch per metric ton (tonne, tn) of paper with PCC at 20 % solids. Some filler samples were only pretreated with swollen cationic starch and some were pretreated with swollen starch and anionic coadditive.

[0111] Coadditive used for PCC pretreatment with swollen cationic starch: anionic micropolymer (TELIOFORM M305<sup>®</sup>, trade-mark of BASF). The treatment of PCC was done by mixing swollen cationic starch and anionic micropolymer with PCC. Different addition orders were used and while the swollen cationic starch dose was fixed at 5 kg/tonne paper, the anionic micropolymer doses were 0.05 % as received material/dry PCC weight and 0.1 % as received material/dry PCC weight.

[0112] Internal starch: Cationic potato starch. Dry starch powder was mixed with water to a 1% solids slurry, which was then cooked at 97 °C with mixing. Cooked cationic starch was used at 8 kg/paper tonne by mixing it with pulp furnish. Retention aid: 0.2 kg/paper tonne of cationic polyacrylamide (CPAM) was used for retention.

#### Example 5

[0113] Table 1 presents the properties of the sheets made with only swollen starch treated PCC and swollen starch followed by anionic micropolymer treated PCC. Anionic micropolymer doses were 0.05 – 0.1% as received material/dry PCC weight. The sheets having anionic micropolymer in PCC pretreatment show better strength properties – tensile, internal bond, bending stiffness – compared to swollen starch alone treated PCC. The best strength performance was achieved with 0.1% anionic micropolymer dose. This would allow a 6% unit filler increase without loss in strength properties.

**TABLE 1**

	PCC content, %	Tensile Index, Nm/g	Internal Bond, J/m <sup>2</sup>	Bending stiffness, mNm
PCC treated with 5kg/tn	19,3	28,0	235	0,18
SST				
PCC treated with 5kg/tn	19,7	28,5	257	0,20
SST and 0.05% AMP	23,6	26,5	239	0,18
PCC treated with 5kg/tn	20,4	33,5	278	0,24
SST and 0,1% AMP	25,2	29,8	267	0,20

[0114] PCC: precipitated calcium carbonate, SST: cationic swollen starch, AMP: anionic micropolymer.

[0115] Tensile and stiffness values are geometrical averages from machine and cross directions.

**Example 6**

[0116] Table 2 presents the properties of paper sheets made with only swollen starch treated PCC, and swollen starch and anionic micropolymer treated PCC using different addition orders: PCC treated with swollen starch followed by anionic micropolymer and anionic micropolymer treated PCC followed by swollen starch.

The presence of anionic micropolymer improves the strength properties of the sheets made with swollen starch treated PCC independent of the addition order.

**TABLE 2**

	PCC content, %	Tensile Index, Nm/g	Internal Bond, J/m <sup>2</sup>
PCC treated with 5kg/tn SST	19.3	28.0	235
PCC treated with	20.4	33.5	278
1) 5kg/tn SST and			
2) 0.1% AMP	25.2	29.8	267
PCC treated with	21.1	32.4	281
1) 0.1 % AMP and			
2) 5kg/tn SST	25.9	28.7	258

[0117] PCC: precipitated calcium carbonate, SST: cationic swollen starch, AMP: anionic micropolymer

[0118] Tensile values are geometrical averages from machine and cross directions.

### Example 7

[0119] The microscope images in Figure 6 illustrate how starch granules swell and how the viscosity increases until it starts to decrease due to rupture of swollen starch granules. The images represent samples of potato starch at 25 °C, 56 °C, 60 °C, 66 °C and 95 °C.

[0120] For the purpose of this invention, swollen starch refers to the condition at which most of the granules have started to swell as shown in the 56 °C image up to to the point where large swollen granules are still visible as seen in the 66 °C image. Thus, the viscosity curve, together with microscopic images, can be used to determine when a starch is sufficiently swollen for use in preparing the filler suspension of this invention. The maximum viscosity area in FIG. 5 is where most of the starch granules are swollen but not ruptured. The temperature range within which useful swollen starch granules can be obtained is in a range that extends from the peak region of FIG. 5 +/- 10 °C. Preferably, the temperature at which the raw starch suspension is heated to create a swollen starch is between the peak

temperature and the peak temperature of Fig. 5 plus 10 °C, where all the starch granules are swollen and all unswollen granules eliminated.

### Example 8

[0121] The handsheet making process was similar to that described previously.

The raw materials used in the sheet making were following:

[0122] Fiber: 100 % eucalyptus used as pulp, refined to SR 30 (at 20 °C) using a Valley Beater lab refiner.

[0123] Filler: precipitated calcium carbonate (ALBACAR<sup>®</sup> LO PCC) from Specialty Minerals Inc., average particle size of 2.1 µm. The PCC content in the sheets varied between 20.4 % and 25.5 % by weight. The PCC is used 1) without any pretreatment, 2) pretreated using only swollen starch and 3) pretreated with anionic micropolymer and raw starch.

[0124] Starch used for PCC pretreatment: Cationic corn starch, which was used in two ways:

[0125] 1. Prepared by mixing dry cationic starch powder with water to make 3% solids slurry and used as such with co-additive, the starch being in granule form.

[0126] 2. Used as swollen starch by first preparing 3% starch slurry by mixing dry starch powder with water and then the slurry heated up to 77 °C under mixing. The PCC pretreatment with swollen starch was done by mixing 5 kg/paper tn of swollen starch with PCC at 20% solids.

[0127] Co-additive used for PCC pretreatment with raw starch granules: anionic polymer (Telioform<sup>®</sup> M305, trade-mark from BASF, marketed as a “micropolymer”). The treatment of PCC was done by first mixing the Telioform<sup>®</sup> with the PCC followed by addition of cold raw starch slurry. The Telioform<sup>®</sup> M305 dose was 0.04 kg/tn paper. The raw cationic starch dose was 5 kg/tn paper.

[0128] Internal starch: Cationic corn starch. Dry starch powder was mixed with water to arrive at a 1 % solids slurry, which was then cooked at 97 °C under mixing. Cooked cationic starch was used 8 kg/tn paper as internal starch by mixing it with pulp furnish.

[0129] Retention aid: Additionally 0.15 kg/paper tn cationic polyacrylamide (CPAM) and 1.5 kg/paper tn silica were used for retention.

[0130] As shown in FIG. 7, PCC pretreatment with swollen starch improves paper strength compared to papers made without such pretreatment.

[0131] Further improvement can be achieved by enhancing the interaction between cationic starch and cationic PCC using anionic micropolymer. The cationic starch can even be raw as shown in the example. Similar behaviour can be seen in stiffness in FIG 8.

### Example 9

[0132] A 0.3% concentration stock was prepared by mixing internal cationic starch with pulp furnish followed by pretreated PCC (or in case of baseline standard PCC without any pretreatment). Before forming paper sheets, a retention aid was added to the stock. The 80 g/m<sup>2</sup> wood-free handsheets were made using a dynamic sheet former (DSF) followed by dynamic sheet pressing and then drying at 120 °C. Prior to paper testing the paper sheets were calendered under the same conditions and then conditioned at 50% RH and 22 °C.

[0133] The raw materials used in the sheet making were following:

[0134] Fiber: 100 % eucalyptus used as pulp, refined to SR 30 (at 20 °C) using a Valley Beater lab refiner.

[0135] Filler: precipitated calcium carbonate (ALBACAR® LO PCC) from Specialty Minerals Inc., average particle size of 2,3 µm. Filler amount in the sheets were adjusted to two levels, 20 % and 25 % by weight.

[0136] Swollen starch used for PCC pretreatment: Cationic corn starch. Swollen starch was prepared by mixing dry cationic starch powder with water to make 3 % solids slurry, which was then heated up to 75 °C under mixing. Cationic swollen starch was used for PCC pretreatment by mixing 5 kg/paper tn of swollen starch with PCC at 20 % solids. Some filler samples were only pretreated with swollen starch and some were pretreated with swollen starch and co-additive.

[0137] Co-additives used for PCC pretreatment with swollen starch: The treatment of PCC was done by mixing swollen starch and co-additive with PCC. Different addition orders and co-additive amounts were used. Swollen starch amount was kept fixed 5 kg/tn of paper. Mixing time for each component was 1 min. Tested co-additives were: carboxymethylcellulose (CMC), polyacrylic acid, soy polymer and nanocellulose.

[0138] Internal starch: Cationic corn starch. Dry starch powder was mixed with water to get a 1 % solids slurry, which was then cooked at 97 °C under mixing. Cooked cationic starch was used 8 kg/paper tn as internal starch by mixing it to pulp furnish.

[0139] Retention aid: Additionally 0,2 kg/paper tn cationic polyacrylamide (CPAM) was used for retention.

[0140] Table 3 presents the tensile strength improvement achieved with PCC filler pretreatment compared to baseline condition without any PCC treatment. PCC filler was either pretreated with swollen starch alone, or with swollen starch and additional co-additive. Tensile strength comparison is done at equal ash level.

[0141] Using the technique described previously, the swollen starch treatment alone gave on average 7.4 % improvement in tensile strength compared to baseline without PCC treatment. By using additional co-additive with swollen starch such as carboxymethylcellulose or polyacrylic acid, tensile strength can be slightly more improved as shown in the Table 3. Use of nanocellulose as co-additive in swollen starch PCC treatment can improve strength properties significantly as also shown in Table 3.

**TABLE 3**

Co-additive	Additive amount		Addition order into PCC	Tensile index /
	kg/paper tn	%/dry PCC		Breaking length improvement vs. baseline
				%
<b>Swollen starch treatment alone (no co-additive)</b>	-	-	sst	<b>7,4</b>
Soy polymer	0,5 (dry)		co-additive + sst	9
Carboxymethylcellulose Finnfix 30	2 (dry)		co-additive + sst	9,4
Polyacrylic acid Acumer		0,15 (as received solution)	co-additive + sst	9,5
Nanocellulose Microfibrillated cellulose	50 (dry)		co-additive + sst	45

[0142] PCC: precipitated calcium carbonate, SST: cationic swollen starch

[0143] Tensile index values are geometrical averages from machine and cross directions.

### Example 10

[0144] A 0.5 % concentration stock was prepared by mixing internal cationic starch with pulp furnish followed by pretreated PCC (or in case of baseline standard PCC without any pretreatment). Before forming paper, a retention aid was added to the stock. The 80 g/m<sup>2</sup> wood-free handsheets were made using a Formax sheet

former, followed by dynamic sheet pressing and then drying at 120 °C. Prior to paper testing the paper sheets were conditioned at 50% RH and 23 °C and calendered from both sides first at 180 psi and then both sides at 220 psi.

[0145] The raw materials used in the sheet making were following:

[0146] Fiber: 100 % eucalyptus used as pulp, refined to SR 30 (at 20 °C) using Valley Beater lab refiner.

[0147] Filler: precipitated calcium carbonate (ALBACAR® LO PCC) from Specialty Minerals Inc., average particle size of 2,3 µm. Filler amount in the sheets were adjusted to two levels, 20 % and 25 % by weight.

[0148] Swollen starch used for PCC pretreatment: Cationic corn starch. Swollen starch was prepared by mixing dry cationic starch powder with water to make a 1% solids slurry, which was then heated up to 75 °C under light mixing in a starch cooker. Cationic swollen starch was used for PCC pretreatment by mixing 5 kg/paper tn of swollen starch with PCC at 20 % solids. Some filler samples were only pretreated with swollen starch and some were pretreated with swollen starch and co-additive.

[0149] Co-additive used for PCC pretreatment with swollen starch: The treatment of PCC was done by mixing swollen starch and co-additive with PCC at temperature 55 °C. Different addition orders and co-additive amounts were used. Mixing time for each component was 1 min. After all components were mixed with PCC, the blend was heated up to 70 °C under constant low shear mixing.

Tested co-additives: anionic aluminium hydroxide, natural gum, silica, bentonite, polyvinyl alcohol (PVA), PVAm, biopolymer and several anionic polymers.

[0150] Internal starch: cationic corn starch. Dry starch powder was mixed with water to get a 0,5 % solids slurry, which was then cooked at 95 °C under low mixing in a starch cooker. Cooked cationic starch was used at 8 kg/paper tn as internal starch by mixing it to pulp furnish. In one of the examples, cooked cationic starch was used at 5 kg/tn for PCC pretreatment instead of swollen starch. Cooked starch treatment was done with and without co-additive.

[0151] Retention aid: Additionally 0,2 kg/paper tn cationic polyacrylamide (CPAM) was used for retention.

### **Example 11**

[0152] The method of Example 10 was followed.



[0153] Different addition orders for PCC, swollen starch and co-additive have been tested in lab scale. PCC treatment was done by either first mixing swollen starch with PCC followed by co-additive or by first mixing co-additive with PCC followed by swollen starch.

[0154] The lab scale results, presented in table 4, show that similar strength gain can be achieved independent of addition order when the same co-additive and the same chemical dosages are used. As can be seen, there is no difference whether PCC is treated first with swollen starch or with co-additive.

**TABLE 4**

Co-additive		Additive amount (as received solution)		Addition order into PCC	Tensile index / Breaking length improvement vs. baseline %
		kg/paper tn	%/dry PCC		
Anionic polymer	Fennosil ES325	0,2		co-additive + sst	11
Anionic polymer	Fennosil ES325	0,2		sst + co-additive	11
Anionic polymer	Nalco 61815		0,05	co-additive + sst	11
Anionic polymer	Nalco 61815		0,05	sst + co-additive	13
Anionic polymer	Nalco 61815		0,23	sst + co-additive	47
Anionic polymer	Nalco 61815		0,23	co-additive + sst	48

[0155] PCC: precipitated calcium carbonate, SST: cationic swollen starch

### Example 12

[0156] The method of Example 10 was followed.

[0157] Table 5 presents the tensile strength improvements achieved with PCC filler pretreatment compared to baseline condition without any PCC treatment. PCC filler was either pretreated with swollen starch alone, or with swollen starch and additional co-additive. Comparison is done at equal ash level.

[0158] When the previously described technique of Example 10 was used, swollen starch treatment alone gave on average 9.2 % improvement in tensile strength compared to baseline without filler pretreatment. By introducing co-additive into filler pretreatment with swollen starch the strength performance improved from marginal improvement to more than doubling as shown in the table 5.

TABLE 5

Co-additive	Additive amount		Addition order into PCC	Tensile index / Breaking length improvement vs. baseline
	kg/paper tn			
<b>Swollen starch treatment alone (no co-additive)</b>	-	-	sst	<b>9,2</b>
Anionic aluminium hydroxide	2	(calc. as dry)	co-additive + sst	13
Natural gum Kelzan	1	(calc. as dry)	co-additive + sst	13
Polyvinylamine (PVAm)	1,5	(as received solution)	sst + co-additive	20
Biopolymer EcoSphere 2202	1	(as received solution)	co-additive + sst	22
Silica Eka NP 2180	4	(as received solution)	co-additive + sst	22
Silica Positek 8699	4	(as received solution)	co-additive + sst	23
Silica Eka NP 320	4	(as received solution)	co-additive + sst	25
Silica Eka NP 442	4	(as received solution)	co-additive + sst	26
Silica Eka NP 890	4	(as received solution)	co-additive + sst	28
Bentonite Hydrocol	2	(calc. as dry)	co-additive + sst	25
Polyvinyl alcohol (PVA) Celvol 103	1	(calc. as dry)	sst + co-additive	24
Polyvinyl alcohol (PVA) Celvol 540	1	(calc. as dry)	co-additive + sst	30
Anionic polymer Fennosil ES325	0,2	(as received solution)	sst + co-additive	11
Anionic polymer Fennosil ES210	0,2	(as received solution)	sst + co-additive	29
Anionic polymer Telioform M305	0,2	(as received solution)	co-additive + sst	27
Anionic polymer Nalco 61815	0,5	(as received solution)	co-additive + sst	48
Anionic polymer Nalco 61816	0,6	(as received solution)	co-additive + sst	37

[0159] PCC: precipitated calcium carbonate, SST: cationic swollen starch

### Example 13

[0160] The method of Example 10 was followed.

[0161] PCC pretreatment can be also done with the cooked starch instead of swollen starch, but the strength performance with cooked starch is significantly lower than that using swollen starch. Table 6 shows the results where PCC has been treated with swollen starch alone and with cooked starch alone. In both cases 5kg/tn starch was used. While swollen starch treatment gave 13% improvement in tensile strength, cooked starch gave 3% at equal ash level.

[0162] Similar to swollen starch treatment, the cooked starch filler treatment can also be improved by using co-additive as shown in Table 6. Depending on dosage the performance can be doubled compared to cooked starch treatment alone.

**TABLE 6**

Co-additives with cooked starch	Additive amount		Addition order into PCC	Tensile index / Breaking length improvement vs. baseline
	kg/paper tn			%
<b>Swollen starch treatment alone</b>	-	-	swollen starch	<b>13</b>
<b>Cooked starch pretreatment alone</b>	-	-	cooked starch	<b>3</b>
Polyvinyl alcohol (PVA)	Celvol 540	1 (calc. as dry)	co-additive + cooked starch	9
Silica	Eka NP 890	2 (as received solution)		4
Silica	Eka NP 890	4 (as received solution)	in all cases	12
Bentonite	Hydrocol	2 (calc. as dry)		5

[0163] PCC: precipitated calcium carbonate

[0164] All patents and patent applications cited in this specification are Incorporated by reference as if each individual patent and patent application were specifically and individually fully set forth herein.

[0165] While the claimed subject matter has been described in terms of various embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the subject matter limited solely by the scope of the following claims, including equivalents thereof.

What is claimed is:

1. A filler suspension for use in papermaking, comprising filler particles, ionic starch and a complementary ionic coadditive.
2. The filler suspension of claim 1, wherein the filler particles are selected from the group consisting of clay, talc, synthetic silicates, sodium magnesium alumino silicate, sodium alumino silicate, ground calcium carbonate (GCC), chalk, precipitated calcium carbonate (PCC), ground calcium sulphate (GCS), precipitated calcium sulphate (PCS), titanium dioxide and combinations thereof.
3. The filler suspension of claim 1, wherein the ionic starch is raw starch.
4. The filler suspension of claim 1, wherein the ionic starch is swollen ionic starch.
5. The filler suspension of claim 1, wherein the ionic starch is cooked ionic starch.
6. The filler suspension of claim 1, wherein the ionic starch is cationic.
7. The filler suspension of claim 1, wherein the ionic starch is anionic.
8. The filler suspension of claim 1, wherein the ionic starch is amphoteric.
9. The filler suspension of any one of claims 1 - 8, wherein the ionic starch is selected from the group consisting of corn starch, rice starch, potato starch, cassava starch, tapioca starch, waxy corn starch, wheat starch, sorghum starch and waxy sorghum starch.
10. The filler suspension of claim 4, wherein the swollen ionic starch is formed by heating an aqueous suspension of raw starch at a gel point temperature of the raw starch  $\pm 10$  °C.

11. The filler suspension of claim 4, wherein the swollen ionic starch is formed by heating an aqueous suspension of raw starch in a temperature range from the gel point temperature of the starch to the gel point temperature of the starch plus 10 °C.
12. The filler suspension of any one of claims 1-6 and 8-11, wherein the complementary ionic coadditive is an anionic flocculant.
13. The filler suspension of claim 12, wherein the anionic flocculant comprises a copolymer of acrylamide and sodium acrylate.
14. The filler suspension of claim 13, wherein the complementary ionic coadditive is selected from the group consisting of NALCO 61815, Nalco 61816, Nalco 61830, Fennosil® ES210, Fennosil® ES211, Telioform® M305.
15. The filler suspension of any one of claims 1-6 and 8-11, wherein the complementary ionic coadditive is an anionic inorganic microparticle.
16. The filler suspension of claim 15, wherein the anionic inorganic particle is selected from the group consisting of bentonites, colloidal silicas, sodium borosilicates, aluminium hydroxides or combinations thereof.
17. The filler suspension of any one of claims 1-11, wherein the complementary ionic coadditive is nanocellulose.
18. The filler suspension of any one of claims 1-6 and 8-11, wherein the complementary ionic coadditive is polyvinyl alcohol.
19. The filler suspension of any one of claims 1-11, wherein the complementary ionic coadditive is anionic or amphoteric PVAm.

20. The filler suspension of any one of claims 1-11, wherein the complementary co-additive is a biopolymer.
21. The filler suspension of claim 20, wherein the biopolymer is starch-based.
22. The filler suspension of claim 21, wherein the starch-based biopolymer is EcoSphere®2202 binder.
23. The filler suspension of any one of claims 1-6 and 8-11, wherein the complementary ionic coadditive is anionic polyacrylic acid or sodium salt of polyacrylic acid.
24. The filler suspension of any one of claims 1-11, wherein the complementary ionic coadditive is natural polymer.
25. The filler suspension of claim 24, wherein natural polymers are selected from the group consisting carboxymethylcellulose, natural gums, soy polymers or combinations thereof.
26. The filler suspension of any one of claims 1-25, wherein the the filler particles are precipitated calcium carbonate.
27. A pulp furnish, comprising pulp fiber and a filler suspension of any one of claims 1-26.
28. The pulp furnish of claim 27, further comprising an additive selected form the group consisting of a sizing agent, a dry strength agent, a wet strength agent, a retention aid and other functional chemicals such as an optical brightening agent, a dye, a defoamer, a bioside and combinations thereof.

29. A paper product, comprising the pulp furnish of claim 27 or claim 28.

FIG.1

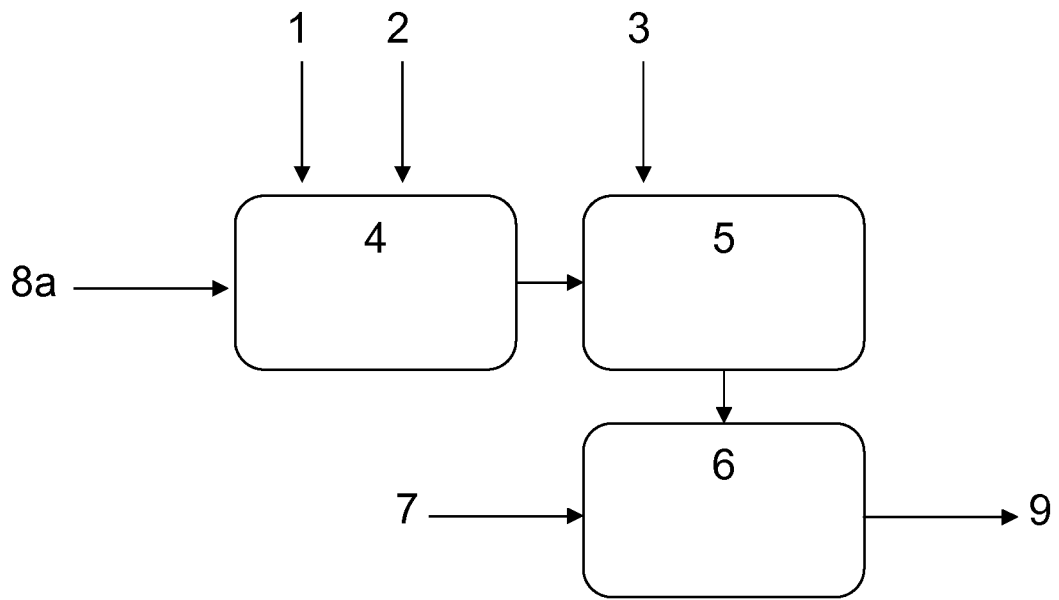


FIG.2

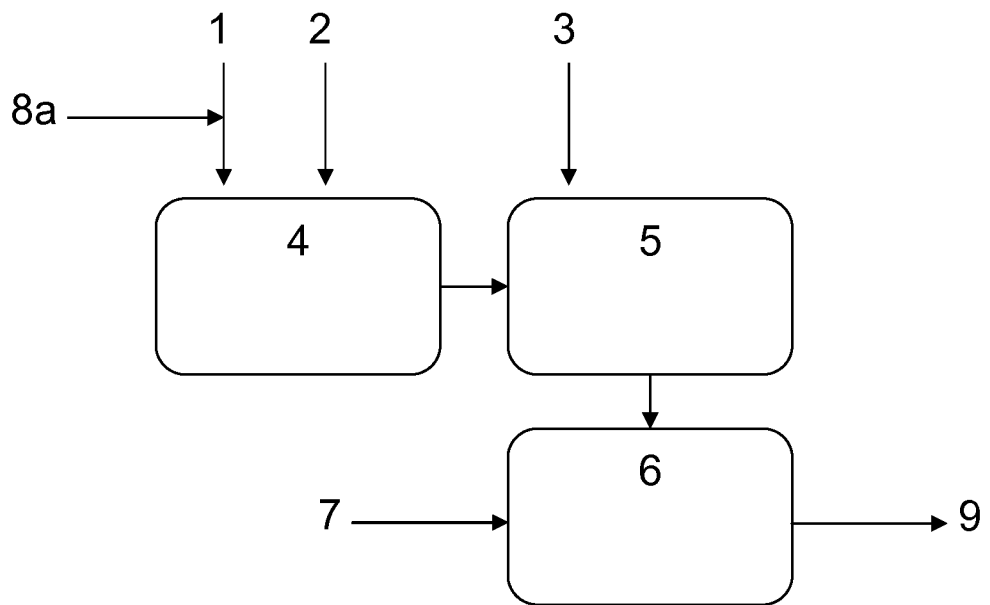




FIG. 3

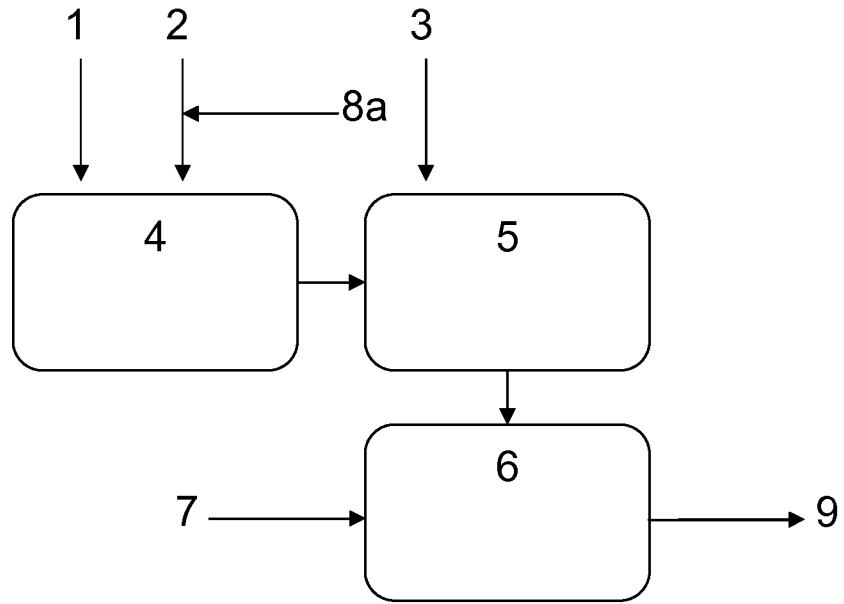
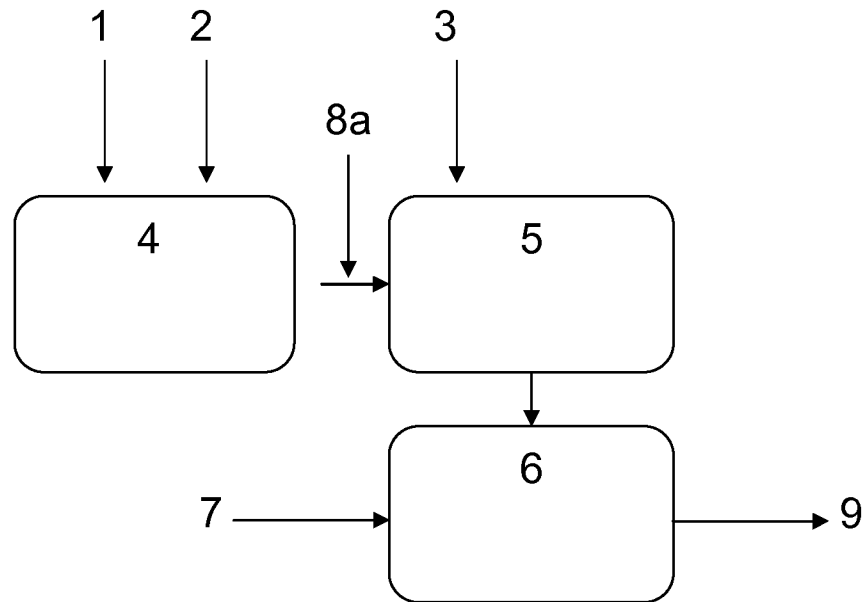


FIG.4



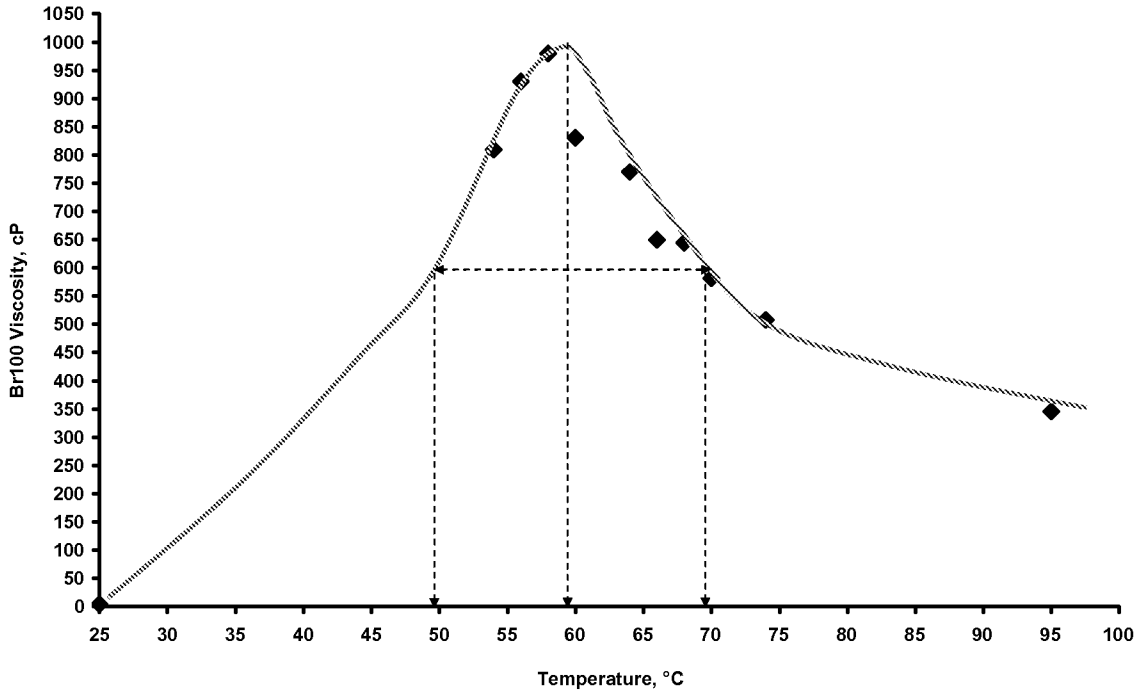


FIGURE 5

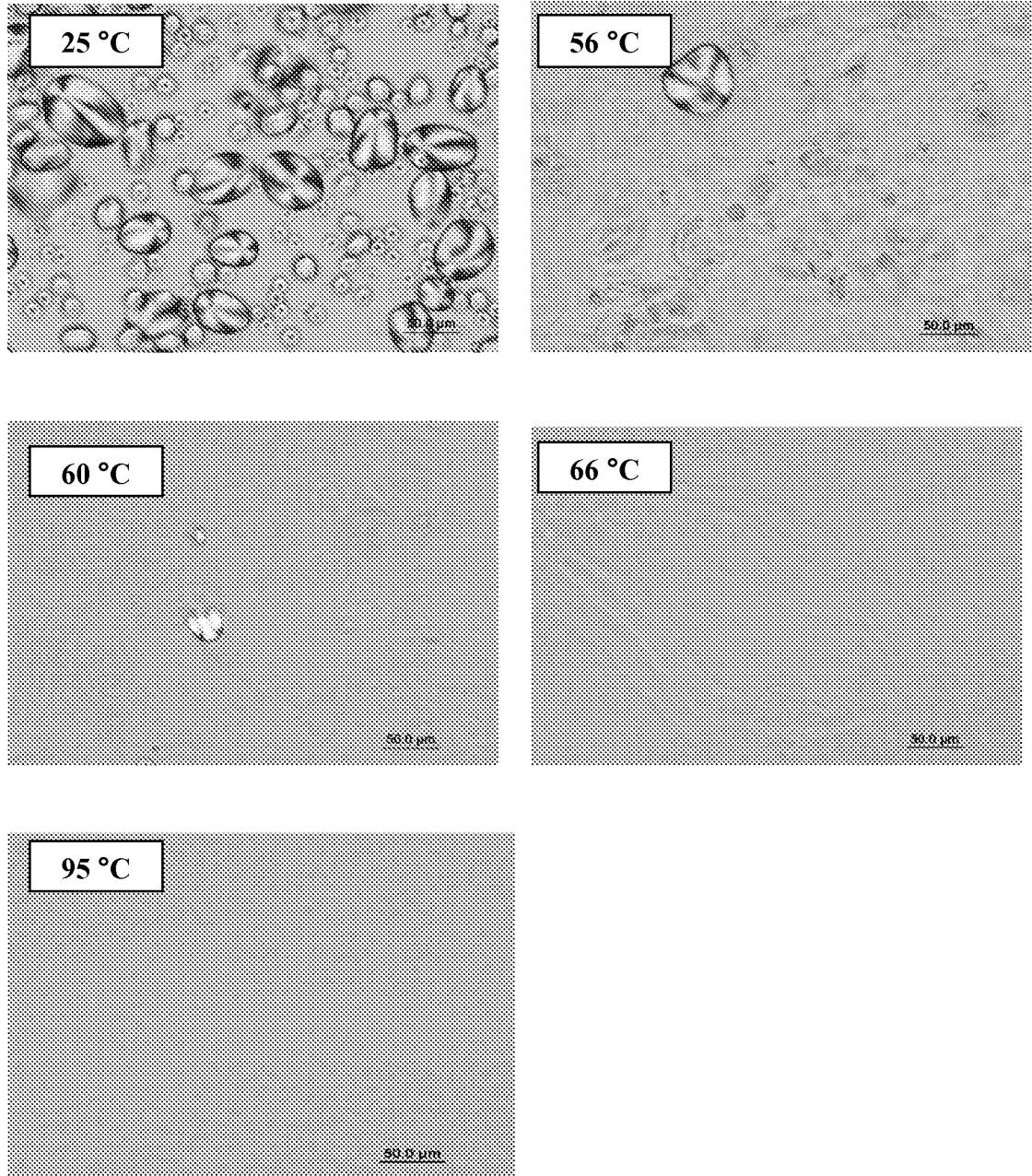


FIGURE 6

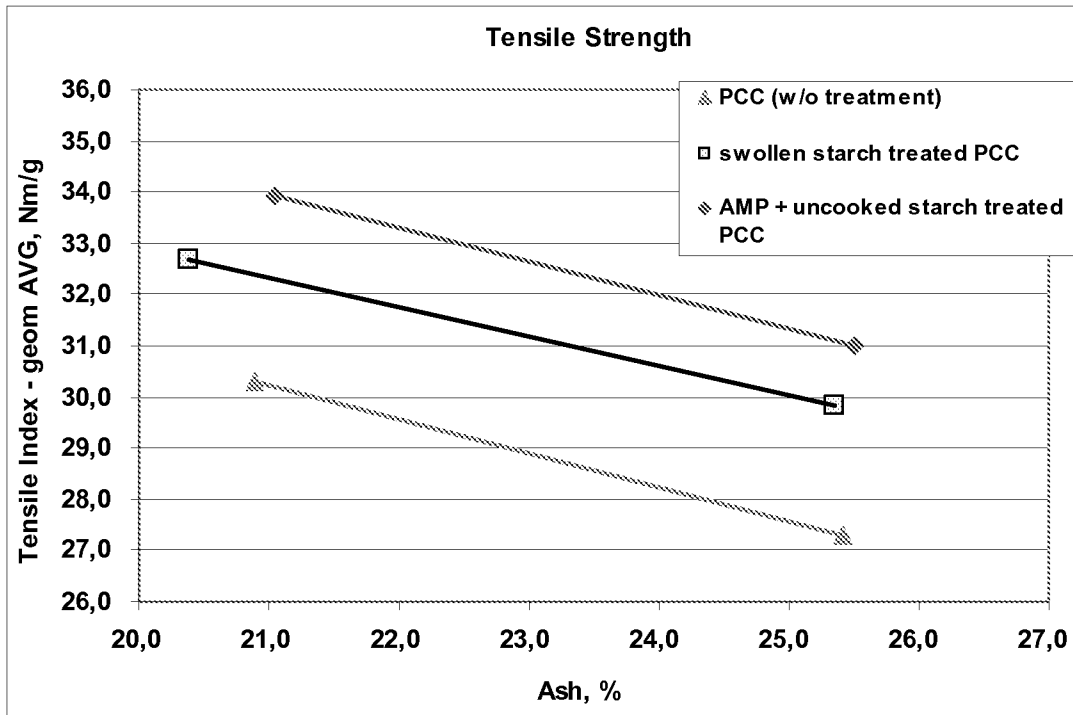


FIGURE 7

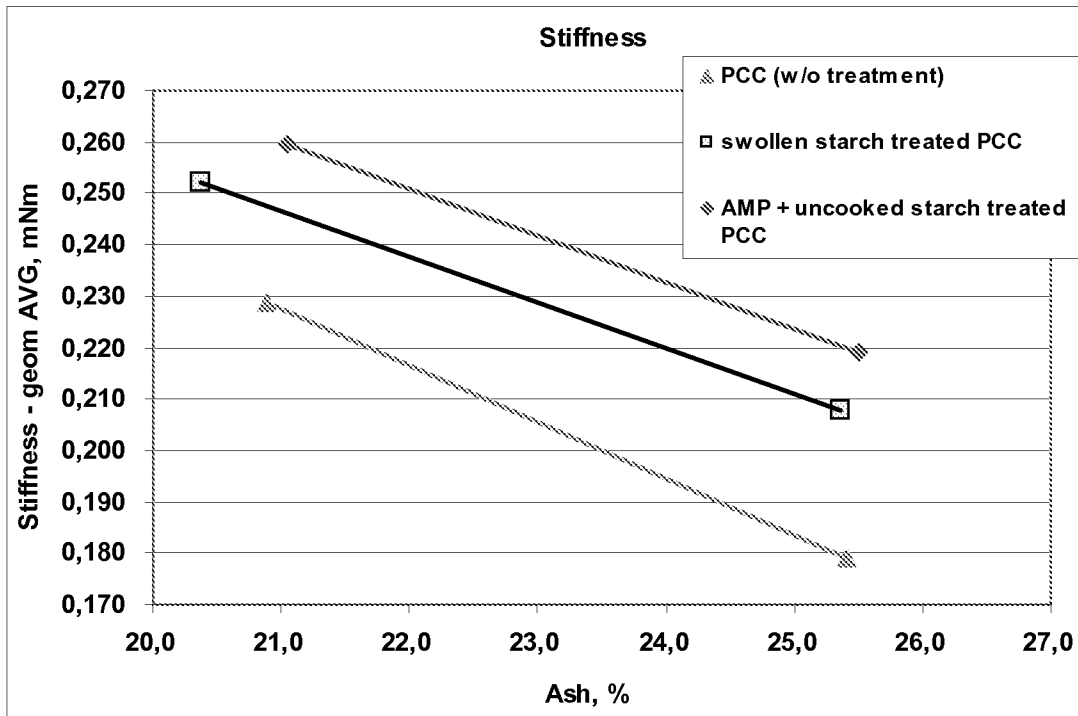


FIGURE 8

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b>				
INV. D21H17/25	D21H17/28	D21H17/29		
D21H17/42	D21H17/63	D21H17/67		
D21H17/34	D21H17/68	D21H17/41		
D21H17/00				
<b>ADD.</b>				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols) D21H				
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				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2003/188738 A1 (LALEG MAKHLOUF [CA]) 9 October 2003 (2003-10-09)	1-16, 23-29		
Y	paragraphs [0003], [0028] - [0031], [0038] - [0044], [0053] - [0064]; claims 12-28	17-22		
X	----- US 6 391 156 B1 (HJALMARSON BO [SE] ET AL) 21 May 2002 (2002-05-21) cited in the application example 1	1,27		
X	----- US 2010/084103 A1 (REINICKE HOLGER [NL]) 8 April 2010 (2010-04-08)  paragraphs [0046], [0071] - [0075]; claims	1,2,5,6, 12,13, 26,27,29		
	----- -/--			
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <span style="margin-left: 200px;"><input checked="" type="checkbox"/> See patent family annex.</span>				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; border: none; vertical-align: top;"> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p> </td> </tr> </table>			<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>
<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>			
Date of the actual completion of the international search	Date of mailing of the international search report			
18 December 2013	03/01/2014			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Koegler-Hoffmann, S			

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	page 3, paragraph 2 page 7, line 19 - page 8, line 17; claims -----	17-22
X	EP 1 143 068 A2 (CIBA SPEC CHEM WATER TREAT LTD [GB]) 10 October 2001 (2001-10-10)	1-9,12, 13,15, 26-29
Y	paragraphs [0004], [0011], [0033], [0066], [0085]; claims -----	17-22

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