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The invention relates to a papermaking agent in liquid form, which comprises (i) cationic starch solution, prepared by cooking a starch mixture comprising a starch component and a water component, and (ii) polymer composition, which has anionic and cationic groups. The polymer composition comprises or originates from at least one of constituents a), b) or c), which has net charge of > 0.1 meq/g, preferably > 0.5 meq/g, at pH 7. The constituent a) is an amphoteric polymer, which comprises a copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, and anionic and cationic groups attached to the copolymer. The constituent b) contains a first polymer, which comprises a first copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, and anionic or cationic groups attached to the first polymer, as well as a second polymer, which comprises groups with opposite charge than the first polymer. The constituent c) contains a first polymer, which comprises a first copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, as well as hydrolytically unstable cationic groups. Constituent a), b) or c) is added to one of the components of the starch mixture or to the starch mixture before the cooking of the starch mixture, and/or constituent a) or b) is added to the cationic starch solution after cooking of the starch mixture.

Keksinnön kohteena on nestemuotoinen paperinvalmistusaine, joka käsittää (i) kationista tärkkelysluosta, joka on valmistettu keittämällä tärkkelysseosta, joka käsittää tärkkelyskomponentin ja vesikomponentin, ja (ii) polymeerikoostumusta, jossa on anionisia ja kationisia ryhmiä. Polymeerikoostumus käsittää tai on peräisin ainakin yhdestä rakenneosasta a), b) tai c), jonka nettovaraus on > 0,1 mekv/g, edullisesti > 0,5 mekv/g pH:ssa 7. Rakenneosa a) on amfoteerinen polymeeri, joka käsittää kopolymeerin, joka käsittää akryyliamidi- ja/tai metakryyliamidimonomeereistä johdettuja rakenneyksiköitä, ja kopolymeeriin liitettyjä anionisia ja kationisia ryhmiä. Rakenneyksikkö b) sisältää ensimmäisen polymeerin, joka käsittää ensimmäisen kopolymeerin, joka käsittää akryyliamidi- ja/tai metakryyliamidimonomeereistä johdettuja rakenneyksiköitä, ja polymeeriin liitettyjä anionisia tai kationisia ryhmiä, sekä toisen polymeerin, joka käsittää vastakkaisen varauksen omaavia ryhmiä kuin ensimmäinen polymeeri. Rakenneosa c) sisältää ensimmäisen polymeerin, joka käsittää ensimmäisen kopolymeerin, joka käsittää akryyliamidi- ja/tai metakryyliamidimonomeereistä johdettuja rakenneyksiköitä, sekä hydrolyytisesti epästabiileja kationisia ryhmiä. Rakenneosa a), b) tai c) on lisätty yhteen tärkkelysseoksen komponenteista tai tärkkelysseokseen ennen tärkkelysseoksen keittämistä, ja/tai rakenneosa a) tai b) on lisätty kationiseen tärkkelysluokseen tärkkelysseoksen keittämisen jälkeen.

PAPERMAKING AGENT AND ITS USE

The present invention relates to a papermaking agent and its use according to the preambles of the enclosed claims.

5

TECHNICAL FIELD

Cationic starch is commonly used in papermaking, for example as a strength additive. Cationic starch can be added to the furnish, where it interacts with the negatively charged fibre surfaces and improves the strength properties of the produced paper. Starch which is added to the furnish should interact as effectively as possible with the fibres and adhere to their surfaces, otherwise it is removed from the process to the circulation water. Starch which does not adhere to the fibre surfaces may cause foaming, high biological oxygen demand (BOD) and chemical oxygen demand (COD) levels in the circulation water, and poor retention and drainage. Poor starch retention with fibres may result in low strength properties of dry paper, and it may also cause linting and dusting problems for paper.

Starch comprises amylopectin and amylose, which are natural polymers build from glucose units. Amylopectin is highly branched and may comprise up to 2,000,000 glucose units, whereas amylose is fairly linear and comprises typically from 300 to 6000 glucose units. Because of its small size amylose is poorly retained on the fibres in the furnish, and amylopectin rich starches are usually preferred in the papermaking. Amylopectin rich starches may be, however, more expensive. Use of starches, which have high amylose content, may also increase the consumption of starch, which naturally increases the process costs.

There is a constant desire to improve the retention of cationic starch to fibres and thus improve the strength properties of the produced paper. Similarly, there is a constant need to cut the costs, i.e. to use cheaper starch and to reduce the amount of used retention chemicals

The object of the present invention is to minimize or even eliminate the disadvantages existing in the prior art.

One object of the present invention is to provide a papermaking agent, with which
5 the retention and the strength of the final paper may be improved.

Typical papermaking agent in liquid form according to the present invention comprises

- (i) cationic starch solution, prepared by cooking a starch mixture comprising a
10 starch component and a water component, and
- (ii) polymer composition, which has anionic and cationic groups,
the polymer composition comprising or originating from at least one of constituents
a), b) or c), which has cationic net charge of > 0.1 meq/g, preferably > 0.5 meq/g,
at pH 7, where the constituent
- 15 a) is an amphoteric polymer, which comprises a copolymer comprising structural
units derived from acrylamide and/or methacrylamide monomers, and anionic
and cationic groups attached to the copolymer,
- b) contains a first polymer, which comprises a first copolymer comprising
structural units derived from acrylamide and/or methacrylamide monomers,
20 and anionic or cationic groups attached to the first polymer, as well as
a second polymer, which comprises groups with opposite charge than the first
polymer, or
- c) contains a first polymer, which comprises a first copolymer comprising
structural units derived from acrylamide and/or methacrylamide monomers, as
25 well as
hydrolytically unstable cationic groups,
- wherein constituent a), b) or c) is added to one of the components of the starch
mixture or to the starch mixture before the cooking of the starch mixture, and/or
- constituent a) or b) is added to the cationic starch solution after cooking of the
30 starch mixture.

Typical use of a papermaking agent according to the present invention is in
papermaking for increasing the retention of cationic starch to the formed web.

Now it has been surprisingly found out that both the efficiency and retention of cationic wet-end starch is clearly and unexpectedly improved when the starch is added to a fibre furnish as a part of a papermaking agent, which comprises also a polymer composition, which has both cationic and anionic groups. The polymer composition may be formed of various constituents, which have a net charge of at least 0.1 meq/g at pH 7, and which may be an amphoteric copolymer, where the cationic and anionic groups are attached to the copolymer, or the constituent be a mixture of cationic and anionic polymers. It is also possible that the polymer composition originate from a constituent, which comprises only cationic groups, when it is united with the starch solution, as long as a part of the cationic groups are hydrolysed to anionic groups during the cooking of starch and preparation of the final papermaking agent. The different constituents comprise structural units derived from acrylamide and/or methacrylamide monomers. It is assumed, without wishing to be bound by a theory that the anionic groups of the amphoteric polymer composition interact with the cationic starch and form large starch/polymer-complexes, whereas the cationic groups of the amphoteric polymer improve the interaction of the formed starch/polymer complex with the fibres in the furnish. Thus the papermaking agent according to the present invention improves the overall retention of the starch, especially the retention of the amylose units, to the fibres. In this manner the strength properties of the final paper are also increased, and the amount of starch in the circulation water of the paper or board production is decreased. The present invention may also enable a decrease in amount of used retention chemicals, whereby the overall cost efficiency of the papermaking process is improved.

Cationic starch solution, which is used in the present invention, is prepared by cooking a starch mixture of comprising a starch component and a water component. Thus, cationic starch solution is a water solution of starch that has been cooked according to methods that are as such well-known for a person skilled in the art. Cooking may be performed with a jet cooker or batch wise or with any other suitable method for cooking starch. The temperature during the starch cooking is typically 95 – 150 °C.

The starch component may be any suitable cationic starch, which is used in paper making, such as potato, rice, corn, waxy corn, wheat, barley or tapioca starch, preferably corn starch, wheat starch, potato starch or tapioca starch, more preferably potato starch. Typically the amylopectin content of the starch component is in the range of 65 – 90 %, preferably 70 – 85 % and the amylose content is in the range of 10 – 35 %, preferably 15 – 30 %. According to one embodiment at least 70 weight-% of the starch units in the cationic starch component has an average molecular weight (MW) over 20 000 000 g/mol, preferably 50 000 000 g/mol, 100 000 000 g/mol.

Starch may be cationised by any suitable method. Preferably starch is cationised by using 2,3-epoxypropyltrimethylammonium chloride or 3-chloro-2-hydroxypropyl-trimethylammonium chloride, 2,3-epoxypropyltrimethylammonium chloride being preferred. It is also possible to cationise starch by using cationic acrylamide derivatives, such as (3-acrylamidopropyl)-trimethylammonium chloride.

Typically cationic starch comprises cationic groups, such as quaternized ammonium groups, and the degree of substitution (DS), indicating the number of cationic groups in the starch on average per glucose unit, is typically 0.01 – 0.20, preferably 0.01 – 0.1, more preferably 0.015 – 0.06. Typically cationic starch has a charge density of 0.06 – 1.0 meq/g, preferably 0.06 – 0.56 meq/g, more preferably 0.09 – 0.35 meq/g.

According to one preferred embodiment of the invention the cationic starch component is non-degraded, which means that the starch component has been modified solely by cationisation, and its backbone is non-degraded and non-cross-linked. Cationic non-degraded starch is of natural origin.

According to first embodiment of the invention the polymer composition comprises a constituent a), which is an amphoteric polymer, which comprises a copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, and anionic and cationic groups attached to the polymer backbone. In

the context of the present application the term “amphoteric polymer” means a polymer, where both cationic and anionic groups are present at pH 7. Thus the constituent a) is one copolymer, which has a main backbone, to which both the cationic and anionic groups are attached. According to one embodiment, the polymer composition may also comprise two or more constituents a), i.e. a plurality of constituents a), which are amphoteric copolymers, but have different chemical and/or physical characteristics. The cationic groups in constituent a) may be hydrolytically stable or they may be hydrolytically unstable.

- 10 According to second embodiment of the invention the polymer composition comprises a constituent b), which contains a first copolymer, which comprises structural units derived from acrylamide and/or methacrylamide monomers, and anionic or cationic groups attached to the first copolymer, as well as a second polymer, which comprises groups with opposite charge than the first copolymer.
- 15 Thus, the constituent b) may comprise two or more different polymers, where the first copolymer(s) comprise(s) anionic or cationic groups attached to the first copolymer backbone and the second polymer(s) comprise(s) groups of opposite charge attached to the second polymer backbone. The cationic groups in constituent b) may be hydrolytically stable or they may be hydrolytically unstable.
- 20 The second polymer may also be a second copolymer, which comprises structural units derived from acrylamide and/or methacrylamide monomers.

- According to third embodiment of the invention the polymer composition comprises a constituent c), which contains a first polymer, which comprises a first copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, as well as hydrolytically unstable cationic groups. Thus, the polymer composition originates from constituent c) having hydrolytically unstable cationic groups. A part or all of the hydrolytically unstable cationic groups may be converted to anionic groups at the conditions prevailing at starch cooking, thus providing an amphoteric polymer, which is present in the final papermaking agent. The obtained amphoteric polymer has both cationic and anionic groups at pH 7. The constituent c) may comprise one or more cationic groups, of which at least one is hydrolytically unstable. Preferably the constituent c) comprises both

hydrolytically unstable cationic groups and hydrolytically stable cationic groups. The constituent c) may be a single first polymer or mixture of first polymers. This means that constituent c) may be a single first polymer, which comprises both hydrolytically stable and unstable cationic groups attached to its backbone, or the
5 constituent c) may be a mixture of at least one first polymer, which comprises hydrolytically unstable cationic groups attached to its backbone, and of at least one second polymer, which comprises hydrolytically stable cationic groups attached to its backbone. In case the constituent c) comprises two or more polymers, they all may be copolymers comprising structural units derived from
10 acrylamide and/or methacrylamide monomers,

According to one embodiment of the invention the hydrolytically unstable cationic groups in constituents a), b) and/or c) may originate from monomers selected from the group consisting of 2-(dimethylamino)ethyl acrylate (ADAM), [2-
15 (acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-dimethylaminoethyl methacrylate (MADAM) and [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl).

According to another embodiment of the invention the hydrolytically stable cationic groups in constituents a), b) and/or c) may originate from monomers selected from the group consisting of [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC), diallyldimethylammonium chloride (DADMAC) and n-vinylformamide. For example,
20 non-ionic n-vinylformamide is hydrolysed during polymerisation in order to give a hydrolytically stable cationic group, attached to the polymer backbone. In the context of the present application the term "hydrolytically stable" means that the cationic group resists chemical decomposition, i.e. hydrolysis, in the presence of water at the conditions prevailing during starch cooking, i.e. at temperature 95 –
25 150 °C.

30 The first polymer of constituent b) may be a dispersion polymer, which comprises cationic polyacrylamide polymerised within an organic coagulant matrix. The dispersion polymers suitable for use in the present invention are synthesised by

using a controlled molecular weight cationic polyacrylamide polymerised within a coagulant matrix. These dispersion polymers are highly structured polymers demonstrating very little linearity. This is largely due to the inclusion of hydrophobic associative groups in the synthesis. The end result is a dispersion
5 polymer system of high cationic charge density polymers having a low molar mass and medium cationic charge density polymers having high molecular weight. These dispersion polymers are free of volatile organic compounds (VOC's) or alkyphenol ethoxylate. The molecular weight of the dispersion polymer may be 5 000 000 – 7 700 000 g/mol and it may have a charge density value of 3 – 6
10 meq/g.

The anionic groups in constituents a) and b) may be derived from monomers, which are selected from the group consisting of acrylic acid, (meth)acrylic acid, maleic acid, crotonic acid, itaconic acid, vinylsulphonic acid, 2-acrylamide-2-
15 methylpropanesulfonic acid, styrene sulfonic acid, vinyl phosphonic acid or ethylene glycol methacrylate phosphate.

In case the polymer composition is obtained by using constituent c), the anionic groups in the polymer composition are derived, at least partly, preferably mainly,
20 more preferably completely, from hydrolytically unstable cationic groups.

According to one embodiment of the invention the polymer composition comprises 10 – 95 weight-%, preferably 15 – 90 weight-%, more preferably 20 – 80 weight-%, still more preferably 25 – 75 weight-%, of structural units derived from acrylamide
25 and/or methacrylamide monomers, calculated from the total dry weight of the polymer composition. Preferably the polymer composition comprises a copolymer of acrylamide with one or more anionic and/or cationic monomers listed above. Also glyoxylated acrylamide copolymers are suitable for use in the present invention. The acrylamide copolymer can be either in acid or in salt form, and it
30 can be linear, branched or crosslinked.

According to one embodiment of the invention the polymer composition comprises or originates from constituent a), b) and/or c), which has a net charge of 0.5 – 5.5

meq/g, preferably 1 – 1.5 meq/g, at pH 7. Thus the net charge of the polymer composition remains positive, which improves the interaction of the formed starch/polymer complex to the fibres. The net charge of a constituent is calculated as the sum of the charges of the cationic and anionic groups. According to one preferred embodiment, the anionic groups in constituents a) and/or b) have a net charge of at least -0.2 meq/g, preferably in the range from -0.3 to -3.0 meq/g, more preferably from -0.4 to -1.5 meq/g, at pH 7.

The polymer composition enhances and increases the cationicity of the starch in the papermaking agent. Typically the increase is 0.01 – 0.2 meq/g, preferably 0.015 – 0.1 meq/g, calculated for dry starch.

According to one embodiment of the invention, the charge ratio of the cationic groups to the anionic groups in the constituent a) or the constituent b) is between 1.1:1 and 20:1, preferably between 1.3:1 and 10:1, more preferably between 1.5:1 and 3:1. The charge ratio may be influenced by selecting the number of anionic and cationic groups in constituents a) and b), and by selecting the number of hydrolytically unstable and stable cationic groups in constituent c). Suitable charge ratio improves the reaction between cationic starch, polymer composition and the fibres in the furnish.

According to one embodiment of the invention the constituents a) and/or b) may be added before the cooking of the starch mixture when the cationic groups of the constituent(s) are hydrolytically stable. The hydrolytically stable cationic groups are not decomposed during the cooking but retain substantially their chemical structure. The constituents a) and b), which comprise hydrolytically stable cationic groups, may alternatively be added to the starch solution after the cooking of the starch mixture.

According to another embodiment of the invention the constituents a) and/or b) may be added to the cationic starch solution after the cooking of the starch mixture when the cationic groups of the constituent(s) are hydrolytically unstable. When the constituents a) or b), which comprise hydrolytically unstable cationic groups

after the cooking of the starch mixture, the risk for decomposition or undesired reactions of the cationic groups is minimised or eliminated.

According to a further embodiment of the invention the constituent c) is added
5 before the cooking of the starch mixture and a part of the cationic groups of
constituent c) are hydrolysed into anionic groups during the cooking. When at least
a part of the cationic groups of constituent c) is converted to anionic groups
through hydrolysis during cooking, a polymer composition comprising both cationic
and anionic groups is provided. Thus the polymer composition, which comprises
10 both anionic and cationic groups, is made "in situ" during the cooking of starch
mixture, and a papermaking agent comprising cationic starch and an amphoteric
polymer composition is obtained.

The constituents a), b) and c) may be added in dry form, i.e. as a powder, or in
15 liquid form, i.e. as a solution. If the constituent a), b) and/or c) is added before the
cooking of the starch mixture, it may be added either to the starch mixture or to
one of the components forming the starch mixture, preferably to the water
component before it is mixed with the starch component.

20 The papermaking agent may comprise polymer composition in amount of 0.1 – 50
weight-%, preferably 0.1 – 30 weight-%, more preferably 0.2 – 15 weight-%,
calculated from total amount of starch.

An object of the present invention is also a method for making a papermaking
25 agent in liquid form, which comprises

- (i) preparing a cationic starch solution by cooking a starch mixture, which
comprises a starch component and a water component, and
- (ii) obtaining a polymer composition, which has anionic and cationic groups,
the polymer composition comprising or originating from at least one of constituents
30 a), b) or c), which has net charge of > 0.1 meq/g, preferably > 0.5 meq/g, at pH 7,
where the constituent

- a) is an amphoteric polymer, which comprises a copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, and anionic and cationic groups attached to the copolymer,
- b) contains a first polymer, which comprises a first copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, and anionic or cationic groups attached to the first polymer, as well as a second polymer, which comprises groups with opposite charge than the first polymer, or
- c) contains a first polymer, which comprises a first copolymer comprising structural units derived from acrylamide and/or methacrylamide monomers, as well as hydrolytically unstable cationic groups,
- wherein constituent a), b) or c) is added to one of the components of the starch mixture or to the starch mixture before the cooking of the starch mixture, and/or - constituent a) or b) is added to the cationic starch solution after cooking of the starch mixture.

According to one embodiment of the invention, the papermaking agent is added to the furnish before the paper or board web formation, preferably to the thick stock. Thick stock is here understood as a fibrous stock or furnish, which has consistency of at least 20 g/l, preferably more than 25 g/l, more preferably more than 30 g/l. According to one embodiment, the addition of the papermaking agent is located after the stock storage towers, but before thick stock is diluted in the wire pit (off-machine silo) with short loop white water.

According to another embodiment of the present invention it is possible to add the papermaking agent to the short circulation.

According to one embodiment of the invention the papermaking composition is especially suitable for use with furnishes with high filler content. It is especially suited for mechanical pulp or for furnishes comprising recycled fibres. According to one preferred embodiment, the furnish may contain at least 30 % of mechanical

pulp or recycled fibre, typically at least 50 % of mechanical pulp or recycled fibre, calculated on basis of dry fibre raw material.

According to one embodiment of the invention the papermaking agent is
 5 advantageous for furnish, which has a cationic demand of $> 100 \mu\text{ekv/l}$, preferably $> 200 \mu\text{ekv/l}$, measured before dosing of the papermaking agent.

The ash content of paper or board product before coating, if any, is $> 10 \%$, preferably $> 15 \%$, more preferably $> 20 \%$. The present invention is suitable for
 10 improving strength of the paper web when producing paper grades including super calendered (SC) paper, ultralight weight coated (ULWC) paper, light weight coated (LWC) paper and newsprint paper, but not limited to these. Typical coated magazine paper, such as LWC, comprises mechanical pulp around 40 – 60 weight-%, bleached softwood pulp around 25 – 40 weight-% and fillers and/or
 15 coating agents around 20 – 35 weight-%. SC paper comprises mechanical pulp around 70 – 90 weight-% and long fibered cellulose pulp around 10 – 30 %. The paper web may comprise fibres from hardwood trees or softwood trees or a combination of both fibres. The fibres may be obtained by any suitable pulping or refining technique normally employed in paper making, such as thermomechanical
 20 pulping (TMP), chemimechanical (CMP), chemithermomechanical pulping (CTMP), groundwood pulping, alkaline sulphate (kraft) pulping, acid sulphite pulping, and semichemical pulping. The paper web may comprise only virgin fibres or recycled fibres or a combination of both. The weight of the final paper web may be 30 – 800 g/m^2 , typically 30 – 600 g/m^2 , more typically 50 – 500 g/m^2 , preferably
 25 60 – 300 g/m^2 , more preferably 60 – 120 g/m^2 , even more preferably 70 – 100 g/m^2 .

The present invention is also suitable for improving strength of the board web when producing paperboard like liner, fluting, folding boxboard (FBB), white lined
 30 chipboard (WLC), solid bleached sulphate (SBS) board, solid unbleached sulphate (SUS) board or liquid packaging board (LPB), but not limited to these. Boards may have grammage from 120 to 500 g/m^2 and they may be based 100 % on primary

fibres, 100 % on recycled fibres, or to any possible blend between primary and recycled fibres.

The invention is described in more detail below with reference to the enclosed
5 schematic drawing, in which

Figure 1 shows schematically the manufacture of the papermaking agent according to the present invention.

10 Figure 1 shows schematically the manufacture of the papermaking agent according to the present invention. Starch component is fed from a storage vessel 101 to a mixing tank 102 where it is mixed with water component and a starch mixture is obtained. Starch mixture is transferred to a cooking stage 103 whereby a starch solution is obtained and transferred to a storage tank 104.

15

Constituent a) comprising an amphoteric copolymer with both anionic and cationic groups can be added before cooking stage 103 or after cooking stage 103 if at least part of the cationic groups are hydrolytically stable. In case all the cationic groups of the amphoteric copolymer are hydrolytically unstable it is added after the
20 cooking stage 103. Possible feeding points for the various constituents of the polymer composition are marked with letters A, B and C.

Constituent b) comprising a first copolymer having cationic or anionic groups attached to it and a second copolymer having groups of opposite charge attached to it. The first and second copolymer may be added simultaneously or sequentially
25 after each other. If at least part of the cationic groups in constituent b) are hydrolytically stable, both the first copolymer and the second copolymer may be added before the cooking stage 103. In case all the cationic groups in constituent b) are hydrolytically unstable both the first and the second copolymer may be
30 added after the cooking stage 103, or alternatively, the copolymer comprising the anionic groups may be added before the cooking stage 103 and the copolymer comprising the cationic groups may be added after the cooking stage 103.

Constituent c) comprising at least a first copolymer with hydrolytically stable cationic groups is added before the cooking stage 103. During the cooking the hydrolytically unstable cationic groups are converted to anionic groups. The constituent c) comprises preferably also hydrolytically stable cationic groups, which may be attached to the same first copolymer as the hydrolytically unstable cationic groups. The constituent c) may also comprise a second copolymer, which comprises the hydrolytically stable groups.

The constituents, which are added to starch mixture before the cooking stage 103 may be added either to the starch mixture, after the mixing of the starch component and the water component, or to one of the components of the mixture, before they are mixed together. In the latter case, the addition is done preferably to the water component.

15 EXPERIMENTAL

Some embodiments of the invention is described in the following non-limiting examples.

20 EXAMPLE 1

Papermaking agents

In all tests, starch is cationic corn starch, having DS 0.043 and moisture content of 12.2 %. Ash content of the dry starch material is 2.77 %. 10 % starch slurry has pH value of 6. Starch is cooked at 1 % concentration at 97 – 100 °C at atmospheric pressure for 90 min and then cooled to 25 °C.

In order to obtain a papermaking agent comprising cationic starch solution and a polymer composition following polymer constituents are added into starch mixture prior cooking:

30

Alternative 1: Aqueous cationic dispersion polymer of cationic polyacrylamide, CPAM, and poly-DADMAC. Proportion of CPAM is 17.5 weight-% of the dispersion. CPAM comprises 70 mol-% of acrylamide, 26 mol-% of DADMAC and

4 mol-% of cationic acrylate ester monomer. MW of CPAM is about 5 000 000 g/mol and charge density is 3.0 meq/g. Proportion of poly-DADMAC is 17.5 weight-% of the dispersion. Charge density of the poly-DADMAC is 6.2 meq/g and the average molecular weight about 300 000 g/mol. Total polymer content is 35 weight-%. Dry solids content is 38 weight-%. Measured charge density is 4.52 meq/g dry material, at pH 2.9.

Alternative 2: Amphoteric polymer, which is an aqueous solution of co-polymer of acrylamide, APTAC and acrylic acid. Cationicity of amphoteric polymer is 10 mol-% and anionicity 5 mol-% of total monomers. Viscosity of the polymer is 13 700 mPas at 19.4 % concentration at pH 4.0. Charge density is 1.2 meq/g dry product, at pH 3, and 0.6 meq/g dry product, at pH 7.

Alternative 3: Cationic non-hydrolysable polymer for enhancing the efficiency of starch is an aqueous solution of non-thermosetting polyamidoamine-epichlorohydrin co-polymer. Viscosity of the polymer is 45 mPas at 25 % concentration, charge density is 4.2 meq/g dry product, at pH 4.

Retention polymer is commercial cationic polyacrylamide Fennopol K 3400 R (Kemira Oyj). The product is dry powder, which is dissolved at 0.5 % concentration by mixing the powder with water and agitating the solution for 1 h at 25 °C.

Characterisation of furnish and process water

pH, conductivity, turbidity, charge and chemical oxygen demand of furnish and process water samples are characterised by using measurements and devices defined in Table 1.

Table 1. Measurements and devices used for characterisation of the furnish and process water.

Measurement	Device
pH	Knick Portamess, Van London-pHoenix company, Texas, USA
Conductivity	Knick Portamess Knick Portamess, Van London-pHoenix company, Texas, USA
Turbidity	WTW Turb 555 IR, WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany
Charge	Mütek PCD 03, BTG Instruments GmbH, Herrsching, Germany
Chemical Oxygen Demand (COD)	DR Lange Lasa 100, Hach Lange GmbH, Düsseldorf, Germany

- 5 Zeta potential for furnish and process water samples is measured as follows: Pulp samples for zeta potential measurements are diluted to approximately 1% consistency with clear filtrate of paper machine process water. Zeta potential is determined using Mütek SZP-06 System Zeta Potential device (BTG Instruments GmbH, Herrsching, Germany). This device applies a vacuum to draw pulp stock
- 10 against a screen and forms a pad of fines and fibres between two electrodes. A pulsating vacuum causes the aqueous phase to oscillate through the plug, thus shearing off the counterions and generating a streaming potential. The zeta potential is calculated by using the measured streaming potential, conductivity, and the pressure difference. The chemical treatment time, before each
- 15 measurement, was obtained in 5 min.

The fines content of the furnish is measured by employing Dynamic Drainage Jar, DDJ (Paper Research Materials, Inc., Seattle, WA), with 60M wire screen, which has 210 μm diameter screen holes. Consistency of the furnish is approximately 1

20 % and the furnish slurry volume is 500 ml in DDJ experiment. Stirring speed is 1000 rpm and stirring is started 45 s before drainage. 100 g of the screened material is filtrated and weighed after drying.

Characteristics of SC-paper furnish employed in the study are given in table 2. SC-paper furnish comprises approximately 75 % of ground wood pulp and approximately 25 % of long fibre kraft pulp.

5

Table 2. Characteristics of SC-paper furnish employed in the Examples.

SC-paper furnish	Mixing chest furnish	Clear filtrate	White water
pH	7.1	7.6	7.8
Turbidity (NTU)	95	21	23
Conductivity filtrate ($\mu\text{S}/\text{cm}$)	2270	1700	2000
Charge ($\mu\text{eq}/\text{l}$)	-43.9	-50	-41.1
Zeta potential (mV)	-18.7	-	-
Consistency (g/l)	33.8	-	-
Ash content (%)	18.3	-	-
COD (mg/l)	1512	1199	1252
Fines content (%) (60M wire)	49	-	-

Manufacture of Sheets and Their Testing

- 10 SC-paper sheets are formed with Moving Belt Former (MBF), shown in Figure 2. MBF is PC-controlled sheet former which utilises a real paper machine wire. Drainage occurs due to pulsating suction. The wire 1 itself is immobile and a moving perforated belt 2 is arranged under the wire 1, which generates suction effect similar to those occurring at the wire section of a paper machine. MBF forms
- 15 a single sheet 3 instead of continuous paper web. The furnish suspension is added to a mixing vessel 4 with mixer 5 and mixed with fillers and retention chemicals. Drainage begins when the drainage foil 6 moves away and furnish suspension comes into contact with the wire 1. Moving belt 2 wipes water away from the wire 1 and the vacuum box 7 generates suction that pulsates to the wire 1
- 20 when the holes of the moving belt 2 passes the wire.

The wire type employed the study is DL2874 two-layer wire with 5100 m³/(m²h) air permeability. The vacuum is 29 kPa, the stirring speed 2000 rpm, and stirring time 40 s

5

The mixing chest furnish is diluted to consistency of 4.6 g/l % with clear paper machine filtrate. Cationic starch and polymer composition are added to the diluted furnish 3 min before 290 ml of the diluted furnish and 290 ml white water are added to the mixing vessel of the MBF, where the furnish mixture is kept under constant mixing. Filler, which comprises clay and ground calcium carbonate in a ratio of 50:50, is added 20 s before the drainage. The consistency is 6.4 g/l after the filler addition. The retention polymer is added 10 s before drainage. Mixing is stopped approximately 5 s before the drainage. After the sheet formation, the sheets are dried 2 min with a hot plate dryer (Lorentzen & Wettre). After the drying, sheets are pre-conditioned for 24 h at 23 °C in 50% relative humidity.

15

SC-paper paper sheets are calendered once on both sides before paper testing with a nip pressure of 150 kN/m and a temperature of 80 °C.

20 The properties of the paper sheets are measured using the methods and devices disclosed in Table 3. Initial wet web strength is determined from undried fine paper sheets with an ash content of approximately 25 %. The sheets are pressed 5 min at 4.5 bar pressure, and the wet tensile strength is measured immediately after pressing.

Table 3. Methods and devices used for measuring paper sheet properties.

Measurement	Standard, Device
Grammage	ISO 536, Mettler Toledo
Ash content	ISO 1762, Precisa PrepAsh 229
Tensile strength	ISO 1924-3, Lorentzen & Wettre Tensile tester
Scott bond	T 569, Huygen Internal Bond tester

Results

- 5 A line is adjusted to the obtained results. From the line it is possible read comparable tensile strength values and retention polymer consumption at standard retention level of 78.2 % and at standard grammage of 80.8 g/m². Ash content of the produced sheets is 36±1 %. Dosage starch, polymer composition and retention polymer is given in relation to the produced paper. 0-test is
- 10 performed without any addition of starch or polymer composition.

The results for the paper sheets comprising different amounts of starch and various polymer compositions are given in Table 4.

Table 4. Results for Example 1.

System	Tensile index, Nm/g	Tensile energy absorption index, J/kg	Scott Bond, J/m ²	Retention polymer consumption, g/t
0-test	10.3	85	131	280
Cationic starch, 6.4 kg/t	10.3	94	132	223
Alternative 1, 29 g/t + cationic starch, 6.4 kg/t	10.8	101	140	181
Alternative 1, 58 g/t + cationic starch, 6.4 kg/t	10.9	104	138	190
Alternative 2, 256 g/t + cationic starch, 6.4 kg/t	11.4	111	133	153
Alternative 2, 1.6 kg/t + cationic starch, 6.4 kg/t	10.9	106	137	154
Alternative 3, 320 g/t + cationic starch, 6.4 kg/t	10,8	102	133	170
Alternative 3, 1.6 kg/t + cationic starch, 6.4 kg/t	10,3	85	139	191

EXAMPLE 2

5 **Hydrolytic Stability of Amphoteric Polyacrylamides**

Hydrolytic stability of amphoteric polyacrylamides at 100 °C is tested. Amphoteric polyacrylamides, which contain different cationic monomer in the polymer, are used in the stability test. The following polymers are used.

10

Polymer 1: Aqueous solution of co-polymer of 85 mol-% acrylamide, 10 mol-% acryloyloxyethyltrimethylammonium chloride (ADAM-Cl) and 5 mol-% acrylic acid.

15

Polymer 2: Aqueous solution of co-polymer of 85 mol-% acrylamide, 10 mol-% [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC) and 5 mol-% acrylic acid.

Polymer 3: Aqueous solution of co-polymer of 85 mol-% acrylamide, 10 mol-% diallyldimethylammonium chloride (DADMAC) and 5 mol-% acrylic acid.

- 5 Measured values of the polymer solutions are given in Table 5.

Table 5. Properties of the polymer solutions used in Example 2.

Polymer #	Cat. Monomer	Dry solids (%)	Viscosity (mPas)	pH	Charge, pH 3 (meq/g dry)	Charge, pH 7 (meq/g dry)
1	ADAM-Cl	19.8	10 500	3.9	1.20	0.55
2	APTAC	19.4	13 700	4.0	1.21	0.60
3	DADMAC	20.0	5 200	3.8	1.24	0.60

- 10 The polymers are first diluted with 100 mmol/l potassium phosphate buffer, pH 7.4, and then further with water in a manner that concentration of the polymer solutions is 1.00 % and concentration of potassium phosphate is 50 mmol/l. pH of each solution is measured at 25 °C. Solutions are kept in sealed autoclave bottles for 24 hours at 100 °C. The bottles are then cooled and pH measured at 25 °C. Charge densities of the polymers are determined by Müttek PDC 03 pH - particle charge detector (BTG Instruments GmbH, Herrsching, Germany) equipped with Müttek PCD Titrator Three –titrator unit (BTG Instruments GmbH, Herrsching, Germany), using 0.001 M PES-Na as titrant polymer for net cationic polymers and 0.001 N poly-DADMAC as titrant polymer for net anionic polymers, both titrant polymers supplied by BTG Instruments GmbH, Herrsching, Germany. Charge densities are determined at pH 3. The results are given in Table 6.
- 15
- 20

Table 6. Results of hydrolytic stability experiments of amphoteric polyacrylamides.

Polymer #	Cat. Monomer	pH before 24 h at 100 °C	pH after 24 h at 100 °C	Charge, pH 3 (meq/g dry)
1	ADAM-Cl	7.4	7.2	-0.15
2	APTAC	7.3	7.3	1.20
3	DADMAC	7.3	7.3	1.22

- 5 The results show that amphoteric polyacrylamide, which contains ADAM-Cl as cationic monomer loses completely its cationic charge in conditions comparable to conditions prevailing during starch cooking. Amphoteric polyacrylamides, which contain APTAC or DADMAC as cationic monomer, do not show any significant change in their cationic charge.

10

EXAMPLE 3

Hydrolytic stability of cationic dispersion polymer

15 Hydrolytic stability of cationic dispersion polymer is tested at 100 °C. The dispersion polymer is the following:

Cationic dispersion polymer corresponds to Alternative 1 in Example 1.

20 The dispersion polymer is diluted first with 100 mmol/l potassium phosphate buffer, pH 7.4, and then further with water in a manner that concentration of the polymer solution is 1.00 % and concentration of potassium phosphate is 50 mmol/l. A clear transparent solution is obtained. pH of the solution is measured at 25 °C, pH 7.3. Solution is kept in a sealed autoclave bottle for 24 hours at 100 °C. Gel lump is formed in to the bottom of the autoclave bottle during the storage time
 25 at 100 °C. The bottle is then cooled and pH is measured at 25 °C. pH is 7.2. pH of the mixture is adjusted to 2.9 with hydrochloric acid and the mixture is mixed for 10 min with magnetic stirrer. The lump is dissolved during the stirring period. Charge density of the polymer is determined by Mutek PDC 03 pH - particle charge

detector (BTG Instruments GmbH, Herrsching, Germany), equipped with Müttek PCD Titrator Three – titrator unit (BTG Instruments GmbH, Herrsching, Germany), using 0.001 M PES-Na as titrant polymer for net cationic polymer, titrant polymer supplied by BTG Instruments GmbH, Herrsching, Germany. Charge density is
5 4.33 meq/g dry material at pH 2.9.

Charge density of the dispersion polymer decreases by 0.19 meq/g during heating. The decrease shows that a part of the cationic groups of the dispersion polymer are hydrolysed during the heating, whereby the cationic dispersion polymer is
10 changed into an amphoteric dispersion polymer. The formation of amphoteric polymer can be observed by the formation of gel lump and then by dissolution of the lump at pH 2.9. The reason for the lump formation is the formation of poly-ion complex of cationic poly-DADMAC groups and anionic groups of hydrolysed polyacrylamide. The dissolution of the lump is a result of breakage of the poly-ion
15 complex, when the formed carboxylic acid anions turn non-ionic at pH 2.9. Amphotericity can be as low as about 4 mol-% of cationic charges.

Even if the invention was described with reference to what at present seems to be the most practical and preferred embodiments, it is appreciated that the invention
20 shall not be limited to the embodiments described above, but the invention is intended to cover also different modifications and equivalent technical solutions within the scope of the enclosed claims.

CLAIMS

1. Papermaking agent in liquid form, which comprises
- (i) cationic starch solution, prepared by cooking a starch mixture comprising a
 5 starch component and a water component, and
- (ii) polymer composition, which has anionic and cationic groups,
 the polymer composition comprising or originating from at least one of constituents
 a), b) or c), which has net charge of > 0.1 meq/g, preferably > 0.5 meq/g, at pH 7,
 where the constituent
- 10 a) is an amphoteric polymer, which comprises a copolymer comprising structural
 units derived from acrylamide and/or methacrylamide monomers, and anionic
 and cationic groups attached to the copolymer,
- b) contains a first polymer, which comprises a first copolymer comprising
 structural units derived from acrylamide and/or methacrylamide monomers,
 15 and anionic or cationic groups attached to the first polymer, as well as
 a second polymer, which comprises groups with opposite charge than the first
 polymer, or
- c) contains a first polymer, which comprises a first copolymer comprising
 structural units derived from acrylamide and/or methacrylamide monomers, as
 20 well as
 hydrolytically unstable cationic groups,
- wherein constituent a), b) or c) is added to one of the components of the starch
 mixture or to the starch mixture before the cooking of the starch mixture, and/or
 - constituent a) or b) is added to the cationic starch solution after cooking of the
 25 starch mixture.
2. Papermaking agent according to claim 1, **characterised** in that the constituent
 a) or constituent b) is added before the cooking of the starch mixture and the
 cationic groups are hydrolytically stable.
- 30
3. Papermaking agent according to claim 2, **characterised** in that the
 hydrolytically stable cationic groups originate from monomers selected from the
 group consisting of [3-(acryloylamino)propyl] trimethylammonium chloride, [3-

(methacryloylamino)propyl] trimethylammonium chloride, diallyldimethylammonium chloride and n-vinylformamide.

4. Papermaking agent according to claim 1, **characterised** in that the constituent
5 a) or constituent b) is added to the cationic starch solution after the cooking of the starch mixture and the cationic groups are hydrolytically unstable.

5. Papermaking agent according to claim 1, **characterised** in that the constituent
10 c) is added before the cooking of the starch mixture and a part of the cationic groups are hydrolysed into anionic groups during the cooking.

6. Papermaking agent according to claim 4 or 5, **characterised** in that the hydrolytically unstable cationic groups originate from monomers selected from the group consisting of 2-(dimethylamino)ethyl acrylate, [2-(acryloyloxy)ethyl]
15 trimethylammonium chloride, 2-dimethylaminoethyl methacrylate and [2-(methacryloyloxy)ethyl] trimethylammonium chloride.

7. Papermaking agent according to claim 5, **characterised** in that the first polymer of constituent c) is a dispersion polymer, which comprises cationic polyacrylamide
20 polymerised within an organic coagulant matrix.

8. Papermaking agent according to claim 1, **characterised** in that the polymer composition comprises or originates from constituent a), b) or c), which has a net charge of 0.5 – 5.5 meq/g, preferably 1 – 1.5 meq/g, at pH 7.
25

9. Papermaking agent according to claim 1, **characterised** in that the anionic groups in constituents a) or b) have a net charge of at least -0.2 meq/g, from -0.3 to -3.0 meq/g, more preferably from -0.4 to -1.5 meq/g, at pH 7.

30 10. Papermaking agent according to claims 1, 8 or 9, **characterised** in that the charge ratio of the cationic groups to the anionic groups in the constituent a) or the constituent b) is between 1.1:1 and 20:1, preferably between 1.3:1 and 10:1, more preferably between 1.5:1 and 3:1.

11. Papermaking agent according to claim 1, **characterised** in that it comprises polymer composition in amount of 0.1 – 50 weight-%, preferably 0.1 – 30 weight-%, more preferably 0.2 – 15 weight-%, calculated from total amount of starch.

5

12. Papermaking agent according to claim 1, **characterised** in that the polymer composition comprises 10 – 95 weight-%, preferably 15 – 90 weight-%, more preferably 20 – 80 weight-%, still more preferably 25 – 75 weight-%, of structural units derived from acrylamide and/or methacrylamide monomers, calculated from

10 the total dry weight of the polymer composition.

13. Use of a papermaking agent according to any of claims 1 – 12 in papermaking for increasing the retention of starch to the formed web.

15 14. Use according to claim 13, **characterised** in that the papermaking agent is added to the furnish before paper or board web formation, preferably to the thick stock.

PATENTTIVAATIMUKSET

1. Nestemuotoinen paperinvalmistusaine, joka käsittää

(i) kationista tärkkelysliuosta, joka on valmistettu keittämällä tärkkelysseosta, joka
5 käsittää tärkkelyskomponentin ja vesikomponentin, ja

(ii) polymeerikoostumusta, jossa on anionisia ja kationisia ryhmiä,
polymeerikoostumuksen käsittäessä tai ollen peräisin ainakin yhdestä
rakenneosasta a), b) tai c), jonka nettovaraus on $> 0,1$ mekv/g, edullisesti $> 0,5$
mekv/g pH:ssa 7, jossa rakenneosa

10 a) on amfoteerinen polymeeri, joka käsittää kopolymeerin, joka käsittää
akryyliamidi- ja/tai metakryyliamidimonomeereistä johdettuja
rakenneyksiköitä, ja kopolymeeriin liitettyjä anionisia ja kationisia ryhmiä,

b) sisältää ensimmäisen polymeerin, joka käsittää ensimmäisen kopolymeerin,
joka käsittää akryyliamidi- ja/tai metakryyliamidimonomeereistä johdettuja
15 rakenneyksiköitä, ja polymeeriin liitettyjä anionisia tai kationisia ryhmiä,
sekä

toisen polymeerin, joka käsittää vastakkaisen varauksen omaavia ryhmiä
kuin ensimmäinen polymeeri, tai

c) sisältää ensimmäisen polymeerin, joka käsittää ensimmäisen kopolymeerin,
20 joka käsittää akryyliamidi- ja/tai metakryyliamidimonomeereistä johdettuja
rakenneyksiköitä, sekä

hydrolyyttisesti epästabiileja kationisia ryhmiä,

jolloin rakenneosa a), b) tai c) on lisätty yhteen tärkkelysseoksen komponenteista
tai tärkkelysseokseen ennen tärkkelysseoksen keittämistä, ja/tai

25 - rakenneosa a) tai b) on lisätty kationiseen tärkkelysliuokseen tärkkelysseoksen
keittämisen jälkeen.

2. Vaatimuksen 1 mukainen paperinvalmistusaine, **tunnettu** siitä, että rakenneosa

a) tai rakenneosa b) on lisätty ennen tärkkelysseoksen keittämistä ja kationiset
30 ryhmät ovat hydrolyyttisesti stabiileja.

3. Vaatimuksen 2 mukainen paperinvalmistusaine, **tunnettu** siitä, että
hydrolyyttisesti stabiilit kationiset ryhmät ovat peräisin monomeereistä, jotka on

valittu ryhmästä, joka koostuu [3-(akryloyyliamino)propyyli]trimetyyliammoniumkloridista, [3-(metakryloyyliamino)propyyli]trimetyyliammoniumkloridista, diallyyldimetyyliammoniumkloridista and n-vinyyliformamidista.

- 5 4. Vaatimuksen 1 mukainen paperinvalmistusaine, **tunnettu** siitä, että rakenneosa a) tai rakenneosa b) on lisätty tärkkelysseoksen keittämisen jälkeen ja kationiset ryhmät ovat hydrolyyttisesti epästabiileja.
5. Vaatimuksen 1 mukainen paperinvalmistusaine, **tunnettu** siitä, että rakenneosa
10 c) on lisätty ennen tärkkelysseoksen keittämistä ja osa kationisista ryhmistä on hydrolysoitunut anionisiksi ryhmiksi keittämisen aikana.
6. Vaatimuksen 4 tai 5 mukainen paperinvalmistusaine, **tunnettu** siitä, että hydrolyyttisesti epästabiilit kationiset ryhmät ovat peräisin monomeereistä, jotka on
15 valittu ryhmästä, joka koostuu 2-(dimetyyliamino)etyyliakrylaatista, [2-(akryloyylioksi)etyyli]trimetyyliammoniumkloridista, 2-dimetyyliaminoetyylimetakrylaatista ja [2-(metakryloyylioksi)etyyli]trimetyyliammoniumkloridista.
7. Vaatimuksen 5 mukainen paperinvalmistusaine, **tunnettu** siitä, että
20 rakenneosan c) ensimmäinen polymeeri on dispersiopolymeeri, joka käsittää kationista polyakryyliamidia, joka on polymeroitu orgaanisessa koagulanttimatriisissa.
8. Vaatimuksen 1 mukainen paperinvalmistusaine, **tunnettu** siitä, että
25 polymeerikoostumus käsittää tai on peräisin rakenneosasta a), b) tai c), jolla on nettovaraus 0,5 – 5,5 mekv/g, edullisesti 1 – 1,5 mekv/g, pH:ssa 7.
9. Vaatimuksen 1 mukainen paperinvalmistusaine, **tunnettu** siitä, että
30 rakenneosissa a) tai b) anionisten ryhmien nettovaraus on vähintään -0,2 mekv/g, -0,3 – -3,0 mekv/g, edullisemmin -0,4 – -1,5 mekv/g, pH:ssa 7.
10. Vaatimuksen 1, 8 tai 9 mukainen paperinvalmistusaine, **tunnettu** siitä, että rakenneosassa a) tai rakenneosassa b) kationisten ja anionisten ryhmien

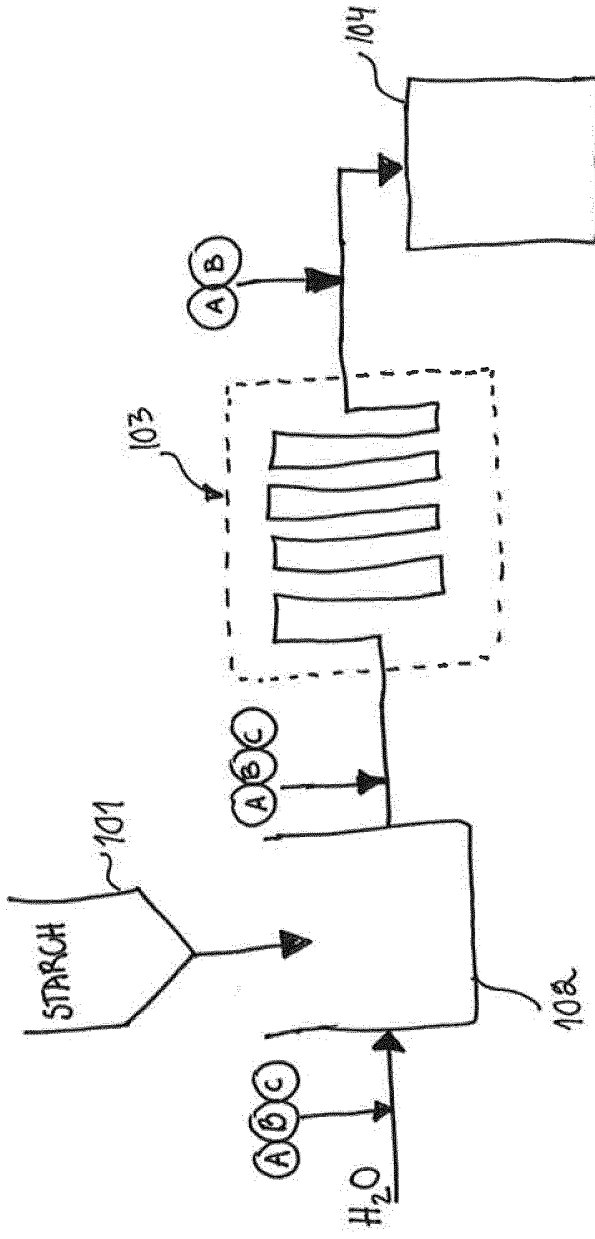
varauksien suhde on välillä 1,1:1 ja 20:1, edullisesti välillä 1,3:1 ja 10:1, edullisemmin välillä 1,5:1 ja 3:1.

11. Vaatimuksen 1 mukainen paperinvalmistusaine, **tunnettu** siitä, että se käsittää
5 polymeerikoostumusta määrässä 0,1 – 50 paino-%, edullisesti 0,1 – 30 paino-%, edullisemmin 0,2 – 15 paino-%, laskettuna tärkkelyksen kokonaismäärästä.

12. Vaatimuksen 1 mukainen paperinvalmistusaine, **tunnettu** siitä, että
10 polymeerikoostumus käsittää 10 – 95 paino-%, edullisesti 15 – 90 paino-%, edullisemmin 20 – 80 paino-%, vielä edullisemmin 25 – 75 paino-%, rakenneyksikköjä, jotka on johdettu akryyliamidi- ja/tai metakryyliamidi-monomeereistä, laskettuna polymeerikoostumuksen kokonaiskuivapainosta.

13. Jonkin vaatimuksen 1 – 12 mukaisen paperinvalmistusaineen käyttö
15 tärkkelyksen retention lisäämiseksi muodostuneeseen rainaan.

14. Vaatimuksen 13 mukainen käyttö, tunnettu siitä, että paperinvalmistusaine lisätään massaan ennen paperi- tai kartonkirainan muodostusta, edullisesti sakeaan massaan.



1/2

FIG. 1

2/2

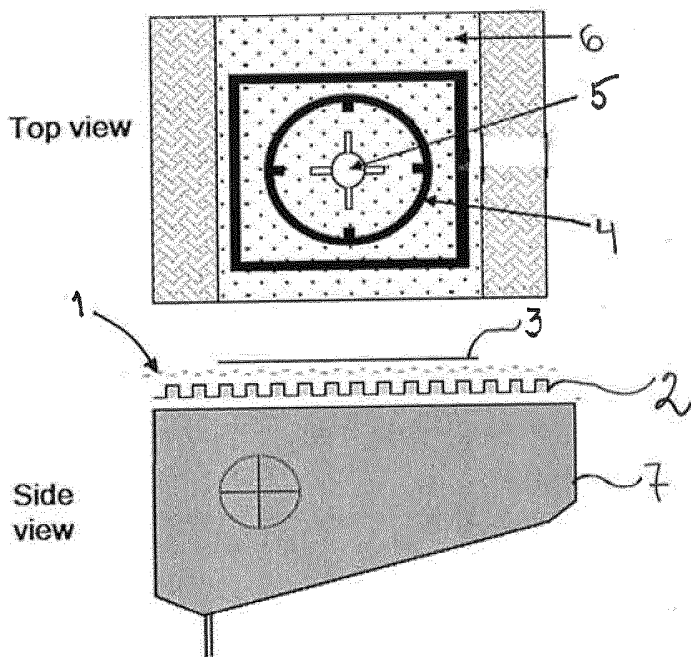


FIG. 2