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(54) **PAPER-MAKING OR NON PAPER-MAKING USE OF A STARCHY COMPOSITION CONTAINING A SELECTED CATIONIC STARCHY MATERIAL**

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(57) **ABSTRACT**

The invention concerns the use, as paper-making additive other than a standard mass additive or water treatment additive, of a starchy composition containing at least a cationic starch material. The invention is characterised in that said composition has: a fixed nitrogen proportion not more than 2%, preferably between 0.1 and 1.9%, said percentages being expressed in dry weight relative to the composition dry weight, and a viscosity, determined in accordance with a test A, of not more than 1600 mPa.s, preferably between 5 and 1500 mPa.s. Some of the starchy compositions, selected on the basis of their fixed nitrogen proportion and their viscosity, are also useful in numerous other fields of application, and in particular as mass additives in paper-making.

PAPER-MAKING OR NON PAPER-MAKING USE OF A STARCHY COMPOSITION CONTAINING A SELECTED CATIONIC STARCHY MATERIAL

[0001] The subject of the present invention is the use, as paper-making additive other than a standard mass additive, or as industrial water treatment additive, of a starchy composition containing a cationic starchy material having particular characteristics of a fixed nitrogen level and of viscosity.

[0002] It also relates to a method for preparing said starchy composition.

[0003] It finally relates, as a novel industrial product, to a starchy composition of the type in question whose cationic starchy material is selected such that said composition can also be used, inter alia, as a standard mass additive.

[0004] The expression "standard mass additive" for the purposes of the present invention is understood to mean any composition which is specifically used:

[0005] at the wet end of the paper machine, and

[0006] in order to improve and capable of improving, alone and directly, the retention of fibers and/or fillers, the dewatering and the physical characteristics of the paper.

[0007] The standard use of cationic starches as mass additives is described for example in patents BE 626,712, EP 139,597, EP 603,727, WO 97/46591 and JP 11-12979 (abstract).

[0008] Commonly, the standard mass additive is used at the earliest in the vessel known to persons skilled in the art by the name of "machine chest" and at the latest at a level situated just before the vessel known to persons skilled in the art by the name of "headbox" of the paper machine itself.

[0009] In a very standard manner, the mass additive is used in a so-called dilute fibrous pulp composition whose suspended matter concentration is generally at most equal to 20 g/l.

[0010] The expression "paper-making additive other than a standard mass additive" is understood to mean any composition which can be used in at least one of the paper-making applications other than that of the abovementioned specific one of standard mass additive and/or be used at least at a level other than the abovementioned levels for introducing a standard mass additive.

[0011] The paper-making additive other than a standard mass additive may be used in particular:

[0012] at the level of the machine chest or upstream thereof, for example at the level of any one of the vessels known to persons skilled in the art by the names of "pulper", "mixing chest", "broke chest", or even immediately after leaving the pulp factory, and/or

[0013] at the very level of the equipment for forming a sheet proper, and/or

[0014] downstream of these sheet forming devices, in particular at the level of creping, surfacing or coating devices, or more generally of any device for treatment, for example spraying or coating, a sheet whose water content is, before treatment, less than about 60%, and/or

[0015] at the level of the preparation of compositions of paper-making additives containing active materials of a nonstarchy nature.

[0016] The expression "paper-making additive other than a standard mass additive" for the purposes of the present invention is understood to mean in particular any composition provided in a solid, liquid or paste form, for example in the form of a free-flowing powder, an aqueous dispersion, an emulsion or a colloidal solution, and useful as agent for reducing inconvenient substances, in particular of an anionic nature, which are contained in water circuits and/or contained on paper-making process equipment.

[0017] It is also understood to mean, inter alia, any composition useful in the preparation of the compositions of sizing agents, which are used in paper-making, in particular as agent for protecting said agents.

[0018] The expression "industrial water treatment additive" for the purposes of the present invention is understood to mean in particular any composition useful in particular as agent for clarifying and/or purifying water obtained from human or industrial activities or intended for said activities, such as for example water intended for human or animal consumption, waste from the textile and leather industries, paper and cardboard industries, mineral extraction industry, agri-foodstuffs industries and slaughterhouses.

[0019] In all the abovementioned fields of application other than the mass additive field, use is commonly made of compositions based on polymers of natural or synthetic origin, in particular of a cationic nature. These may in particular consist of cationic starchy materials as recently described in:

[0020] patents EP 626,022 and CA 2,160,103 relating to their use as agents for reducing inconvenient, in particular anionic, substances contained in paper-making circuits,

[0021] patents WO 97/35068 and WO 99/18288 relating to their use as agents for protecting sizing compositions used in paper-making, and

[0022] patents U.S. Pat. Nos. 5,543,056 and 5,236,598 relating to their use as additives for treating industrial water.

[0023] EP patent 626,022 claims the use, as agent for reducing inconvenient substances in paper-making water circuits, of cationic starches having a charge density which is necessarily very high, namely from 1.5 to 3.5 meqv/g, and preferably from 2 to 3 meqv/g. These ranges correspond to cationic starches having a total nitrogen level of about 2.1 to 4.9%, preferably of about 2.8 to 4.2% (dry weight/dry weight). The method for preparing the cationic starches used for this purpose in the examples of this patent is not at all described, including the botanical origin of the starches tested.

[0024] Taking into account nevertheless the level of cationicity required, it appears clearly that at the industrial stage, such cationic starches can only be reasonably prepared in an adhesive phase as described for example in patent application WO 95/18157 published in the name of the same applicant.

[0025] The examples of this document envisage the preparation of highly cationic potato starch pastes, characterized by a degree of substitution ("DS") of 0.72 and 0.75, this being from highly concentrated reaction media, characterized by a dry matter ("DM") content greater than 50%, of which about half is provided by the cationization agent ("Raisicat 65") alone.

[0026] The very preparation of such highly cationic and highly concentrated compositions in fact involves, according to said examples, a preliminary step of oxidation of the potato starch by hydrogen peroxide.

[0027] However, both intrinsically and at the applicative level, such pastes have a number of disadvantages.

[0028] In the first place, and as confirmed by the analyses carried out by the applicant on products marketed under the name "RAIFIX" by the proprietor of the abovementioned patents EP 626,022 and WO 95/18157, these highly cationic pastes have a relatively low nitrogen fixing level, generally less than 65%. The result is in particular a high residual quantity of cationic reagent and/or of its hydrolysis products in such compositions themselves, which impedes their real efficacy as agents for removing the inconvenient, in particular anionic, substances present in paper-making circuits.

[0029] Moreover, this very partial fixing of the nitrogenous cationic reagent makes it difficult to envisage the use of these pastes as additives for treating industrial water, in particular water intended for human or animal consumption.

[0030] In addition, the high pH of these pastes, generally greater than 9, can pose problems of safety and of corrosion which are inherent to the preparation, to the handling and to the use of alkaline products.

[0031] Finally, the intrinsic characteristics of these pastes are such that they are generally poorly suited:

[0032] because of their relatively high viscosity, to operations of dilution and then of introduction into an aqueous medium, it being possible for this to result in reductions or inconsistencies in the efficacy of these pastes, but also, as a consequence, of the (essentially cationic) starches moreover used in the mass of the paper-making fibers, and/or

[0033] because of their high hydrophilicity, to drying or pregelatinization operations in order to obtain powders or flakes, followed by rehydration of said powders or flakes.

[0034] These disadvantages are in fact amplified for starchy bases of cereal origin (corn, wheat in particular), the preparation or use of such bases in cationic form not at all being exemplified in the abovementioned patents EP 626,022 and WO 95/18157.

[0035] The same is in fact the case in patent WO 99/18288 in the name of the same applicant, which claims the use of starches, also at high levels of cationicity (DS between 0.15 and 1.30, preferably between 0.50 and 0.80), in the preparation of rosin emulsions intended for sizing paper. It is indicated therein that the total nitrogen level of these cationic starches is preferably from 3 to 5%, and ideally 3.5%, it being possible for such products to be advantageously obtained directly according to the method described in the abovementioned patent WO 95/18157.

[0036] Only potato starches having a total nitrogen level of 3.5% are exemplified in this document.

[0037] In the same field of application, i.e. the preparation of compositions of sizing agents, patent WO 97/35068 also recommends the use of highly cationic starches simultaneously having:

[0038] a DS greater than 0.1, preferably between 0.4 and 1.0, and

[0039] a charge density between 0.5 and 3.5 meqv/g, preferably between 1.0 and 2.0 meqv/g.

[0040] Thus, the cationic product used in degraded or liquid form in the examples of this patent have a DS of 0.48 (that is a theoretical fixed nitrogen level of about 2.7-2.8%) and a charge density of 1.32 meqv/g. The botanical nature and the preparation, in particular degradation, conditions are however not specified. In the field of the treatment of industrial water, it has been recently proposed in U.S. Pat. No. 5,236,598, to resort to cationic starches whose DS is preferably between 0.01 and 0.2, that is to say significantly below those claimed in the abovementioned patents. However, such cationic starches should be necessarily combined with hydrolzyed polyacrylamides in order to be effective in the application considered (treatment of paint waste). In addition, the authors only exemplify a nondegraded cationic potato starch, in this case the product HI-CAT® 142 marketed by the applicant, in combination with a polyacrylamide because, according to their assertions:

[0041] 1) starchy bases other than potato starch, in particular corn starch, are not suitable (cf. column 4, 1. 62-66), and

[0042] 2) the molecular weight of the cationic starch is not a critical parameter (cf. column 4, 1. 44-45).

[0043] In the particular field of the treatment of drinking water, it has also been recently recommended to combine, in mixtures, a so-called primary coagulant such as chitosan or a cationic starch with a clay, the latter being present in large proportions in said mixtures.

[0044] The cationic charge of the primary coagulants tested, in particular of the cationic starches, is not expressly mentioned. It is however recalled that chitosan has a high charge density (cf. column 5, 1. 41-45). No reference is moreover made to the possible degradation of the primary coagulant, in particular of a cationic starch, in view of its use.

[0045] On the other hand, the authors prefer here again the basic cationic starches, potato starch, the only cationic starches exemplified.

[0046] The result of the preceding text is that no means exists until now which has simultaneously the advantages of being capable of being:

[0047] effectively used as agent for reducing inconvenient, in particular anionic, substances contained in paper-making water circuits and/or retained on paper-making process equipment, and, if possible, more generally as paper-making additive other than a standard mass additive,

[0048] effectively used as industrial water treatment additive,

[0049] optionally used in other fields, including mass paper-making,

[0050] used in the form of pastes, dilute or otherwise, of aqueous suspensions or of solid forms such as powders or flakes,

[0051] obtained from any starchy bases, including cereals, and

[0052] obtained, in a simple and inexpensive manner, by standard methods of processing, in particular of cationization, of starch materials.

[0053] The applicant company has the merit of having found, after numerous research studies, that such a means could consist in a starchy composition having selected characteristics both in terms of fixed nitrogen level and of viscosity.

[0054] More precisely, the subject of the present invention is the use, as paper-making additive other than a standard mass additive or as water treatment additive, of a starchy composition containing at least one cationic starchy material, characterized in that said composition has:

[0055] a fixed nitrogen level at most equal to 2%, preferably between 0.1 and 1.9%, these percentages being expressed by dry weight relative to the dry weight of the composition, and

[0056] a viscosity, determined according to a test A, at most equal to 1600 mPa.s, preferably between 5 and 1500 mPa.s.

[0057] The test A used to measure the viscosity of said composition is applicable regardless of the form of presentation thereof, liquid, pasty or solid.

[0058] It consists in measuring, by any standard method within the capability of persons skilled in the art, the dry matter (DM) content of said composition and, depending on the case, in diluting said composition with distilled water or in concentrating it by any appropriate means not capable of significantly modifying the average molecular weight of the cationic starchy material which it contains, this being in order to adjust the DM of said composition to a value of 20%.

[0059] After that, the Brookfield viscosity at 25° C. and at 20 revolutions/minute of the resulting composition containing 20% DM is measured in a manner known per se.

[0060] According to one variant, the starchy composition according to the invention is provided in solid form, for example in the form of a free-flowing powder or in liquid form, for example a paste, having a DM of 5 to 65%, preferably of 10 to 50%. This dry matter content may be advantageously greater than 15% and less than 45%, in particular may be between 18 and 40%.

[0061] It should be emphasized that the dry matter content of the composition according to the invention may consist exclusively or almost exclusively of at least one cationic starchy material containing or not other species obtained from cationization but may also contain one or more other components, preferably chosen from starches and derivatives of an anionic or nonionic nature, hydrogenated sugars such as hydrogenated starch hydrolysates and sorbitol, which are optionally cationized, cationic products of non-starchy origin, biocidal agents and other paper-making or non paper-making active materials.

[0062] According to a preferred variant of the present invention, the starchy composition has a fixed nitrogen level of between 0.2 and 1.5% (dry weight/dry weight). Still more advantageously, this fixed nitrogen level is between 0.4 and 1.5% (dry weight/dry weight) and most particularly between 0.5 and 1.5% (dry weight/dry weight).

[0063] Surprisingly and unexpectedly, in particular in view of the teachings of the abovementioned patent EP 626,022, the applicant company has indeed found that starchy compositions having a fixed nitrogen level which is relatively low, i.e. at most equal to 2%, preferably selected between 0.1 and 1.9% and in particular between 0.2 and 1.5%, combined with equally particular viscosity characteristics, could constitute very effective paper-making additives, in particular as agents for reducing inconvenient substances contained in paper-making circuits and/or retained on paper-making process equipment.

[0064] One of the advantages of such starchy compositions having a relatively low fixed nitrogen level is to be capable of being easily and efficiently obtained according to a multitude of variants. The cationization step may be carried out either in an aqueous medium as described for example in EP patent 139,597 or in a dry phase as described for example in FR patent 2,434,821 or in a solvent phase, this being so as to allow one or more nitrogenous groups of an electropositive, or even polyelectropositive, nature to bind to any starchy material contained in said compositions.

[0065] It should be emphasized that the cationic starchy materials which can be used according to the invention may consist of amphoteric products, that is to say of products which are both cationic and anionic. The anionic substituents may, by way of example, be chosen from the group comprising phosphate, phosphonate, sulfate, sulfoalkyl, carboxyl, carboxyalkyl and sulfocarboxyl groups.

[0066] The expression "starchy material" for the purposes of the present invention is understood to mean all starches, of natural or hybrid origin, including those obtained from genetic mutations or genetic engineering. Said starches may in particular be obtained not only from potato, but also from potato with high amylopectin content (waxy potato), corn, wheat, wheat with high amylopectin content (waxy wheat), corn with high amylopectin content (waxy corn), corn with high amylose content, rice, pea, barley or cassava, cuts or fractions which may be made or obtained such as amylose, amylopectin, granulometric fractions known to persons skilled in the art by the terms wheat starch "A" and wheat starch "B", and any mixtures of at least any two of the abovementioned products, for example a mixture of at least one tuber starch (potato starch in particular) and of at least one cereal starch (wheat starch "A", wheat starch "B", corn starch, waxy corn starch in particular) or two cereal starches. The starchy compounds which can be used according to the invention may also consist of flours or other mixtures containing vegetable starch(es) and protein(s), the "starch" components being predominant.

[0067] This may also include starch derivatives, which may, as will be moreover described, be subjected to at least one additional modification treatment prior to, simultaneously with or subsequent to the cationization step.

[0068] This may include in particular derivatives obtained from the hydrolysis of starch, in particular maltodextrins having a Dextrose Equivalent ("DE") at most equal to about 5 such as the product marketed under the name GLUCIDEX® 2 by the applicant, and which are then, in the context of the invention, cationized after the hydrolysis step.

[0069] As mentioned above, the starchy composition which may be used according to the invention has a viscosity, determined according to the test A described above, at most equal to 1600 mPa.s, preferably between 5 and 1500 mPa.s.

[0070] Such viscosities are remarkably low and generally involve a modification treatment, in particular a degradation treatment, of the starchy material contained in said composition, this being, as indicated, either prior to, simultaneously with or subsequent to the cationization step proper.

[0071] This treatment may be carried out by any means, in particular by chemical, enzymatic and/or physical means, known to persons skilled in the art and capable of allowing the production, directly or otherwise, of a starchy composition having a viscosity, determined by the test A, as claimed. It may be carried out continuously or batchwise, in one or more steps, according to a multitude of variants as regards the nature, the quantity or the form of presentation of the means of modification, the reaction temperature and time, the water content of the reaction medium, the nature of the substrate (starchy material already cationized or not yet cationized), and the like. This may include in particular a fluidizing treatment by the chemical route, in an aqueous medium or in a dry phase, such as those mentioned or described in EP patent 902,037 in the name of the applicant.

[0072] This may also include, advantageously, an enzymatic fluidizing treatment (also called enzymatic conversion or liquefaction), it being possible for the latter to be carried out, for example, according to the teachings of FR patent 2,149,640 published by the applicant.

[0073] These enzymatic means include enzymes, thermostable or otherwise, of the α-amylase type of bacterial, fungal or other origin.

[0074] This may also include, in another advantageous manner, a treatment which makes it possible to efficiently convert the cationic starchy material, in an aqueous medium, by means of enzymes chosen from the group comprising branching enzymes (EC 2.4.1.18) and cyclodextrin glycosyltransferases or "CGTases" (EC 2.4.1.19). The branching enzymes may in particular consist of starch or glycogen branching enzymes isolated from algae or from bacteria, such as those whose use is described in patents WO 00/18893 and WO 00/66633 in the name of the applicant.

[0075] The applicant company observed that the cationic starchy materials treated, before, during or after cationization, with a branching enzyme exhibited, in general, a stability during storage which was further improved compared with those treated with an alpha-amylase. Without wishing to be bound by any theory, the applicant thinks that this remarkable result is due, at least in part, to the fact that a treatment with a branching enzyme makes it possible to obtain more homogeneous hydrolzyed starchy materials, i.e. in particular whose resulting constituent saccharides have molecular masses which are distributed on a Gaussian curve which is globally more regular, more symmetrical and narrower than that obtained with an alpha-amylase. Preferably, the treatment with a branching enzyme is carried out after the cationization step and it is in fact remarkable and surprising that the presence of cationic groups, of a relatively large size, does not hamper the oligo- or polysaccharide chain transfer action of such enzymes.

[0076] The use of thermostable enzymes allows, if desired, the practice of enzymatic liquefaction at temperatures of the order of 90-100° C., conditions which are particularly advantageous for producing quality colloidal solutions, especially in terms of solubility and stability of the viscosity.

[0077] The modification treatment may also, by way of nonlimiting examples, involve fluidification combining an acid and an enzymatic route with a dextrinization treatment or with a pyroconversion treatment.

[0078] All the abovementioned means are applied to the starchy material (already cationized or not) already contained or before being contained in the composition according to the invention, such that the weight-average molecular mass of said material is generally less than 10^7 daltons, preferably less than 5×10^6 daltons.

[0079] Advantageously, this weight-average molecular mass is between 10^4 and 4×10^6 daltons.

[0080] The applicant company has indeed observed that the use of degraded cationic starchy materials having molecular masses in the abovementioned ranges ensured not only very good efficacy of the compositions according to the invention in particular as paper-making additives other than standard mass additives or industrial water treatment additives but also a very good stability thereof in terms of behavior during operations of handling, storage, transport, pumping and introducing into/over the application media such as for example paper-making circuits and equipment, emulsions of sizing agent, creping, surfacing or coating compositions, ore suspensions or water intended for consumption.

[0081] According to another variant of the composition which can be used according to the invention, it has a charge density index "CDI" greater than 600, preferably greater than 650, said value being determined according to the formula below:

$$CDI = \frac{\text{charge density of the composition in } \mu\text{eqv/g}}{\text{total nitrogen level of the composition in } \%}$$

[0082] The charge density is measured on a particle charge detector as described below in EXAMPLE 1.

[0083] The total nitrogen level is measured according to the standard KJELDAHL method and expressed in dry weight over the dry weight of the composition.

[0084] The abovementioned CDI value reflects the efficacy with which the nitrogenous groups, provided during the cationization step, effectively bind to the starchy material contained in said composition, and thereby increase the charge density thereof.

[0085] The applicant company found that compositions according to the invention having a CDI value of between 660 and 800 could very advantageously be used as paper-making additives or industrial water treatment additives.

[0086] Such CDI values are very significantly higher than the values found or deduced for the prior art products and which are generally less than 600, or even less than 500, because in particular of the large presence of unbound nitrogenous species (cationic reagent and its hydrolysis products) in these products, making them moreover inexploitable or little exploitable in certain applications such as the treatment of drinking water.

[0087] That is the case in particular for compositions of the abovementioned "RAIFIX" range, but also of the highly cationic starch exemplified in the abovementioned patent WO 97/35068 and for which a DS of 0.48 is reported, that is a theoretical fixed nitrogen level of about 2.7% -2.8% (dry weight/dry weight) for a charge density of 1.32 meqv/g, that is 1320 μeqv/g. Such a product therefore has a CDI value of about 1320/4, that is about 330.

[0088] The pH of the composition according to the invention may be as high as, or may even exceed, the value of 10, but according to another preferred variant, the starchy composition in accordance with the invention has a pH of less than 9, preferably of between 4 and 8.5, said pH being measured in a standard manner, this being on a composition whose DM has been adjusted (if necessary) to a value of 20% as described for the preparation of a sample according to the abovementioned test A.

[0089] These pH ranges also categorically distinguish the claimed compositions of the prior art products of the "RAIFIX" range, which are a lot more alkaline and therefore potentially more harmful and corrosive both for humans and for equipment. These pH ranges therefore also make it possible to envisage fields of application other than those reserved, in practice, for said prior art products.

[0090] Accordingly, a novel means is available which can be effectively used as a paper-making additive other than a standard mass additive and as industrial water treatment additive, in particular as agent for reducing the inconvenient substances contained in water circuits and/or retained on process equipments, for paper-making or otherwise, or as additive in the preparation of compositions of paper sizing agents.

[0091] In addition, as observed by the applicant, this means is particularly well suited, in particular:

[0092] as additive in the preparation of compositions for creping, surfacing or coating paper,

[0093] as additive in the preparation of compositions containing optical brighteners, colorants and/or synthetic polymers such as polyacrylamides or polyvinylamines, said compositions being themselves capable of being used as paper-making additives other than standard mass additives.

[0094] The weight ratios of synthetic polymer(s)/cationic starchy material(s) may be between 1/100 and 100/1, said ratios being expressed by dry weight of synthetic polymer(s) on the one hand and of cationic starchy material(s) on the other hand.

[0095] Advantageously, this means consists in particular, as will be moreover exemplified, of a starchy composition as described above and characterized in that it has:

[0096] a fixed nitrogen level between 0.4 and 1.5% (dry weight/dry weight), and

[0097] a viscosity, determined according to said test A, between 10 and 800 mPa.s.

[0098] The applicant company has in particular found that on the one hand, this nitrogen level could advantageously be between 0.5 and 1.5% and in particular between 0.6 and 1.5% and on the other hand, this viscosity could advantageously be in the range going from 50 to 700 mPa.s.

[0099] Surprisingly, it was observed that compositions which can be used according to the invention, fluidified and having, according to the test A, a viscosity in this preferred range, made it possible to reach, compared with compositions according to the invention having the same fixed nitrogen level but a higher viscosity, a higher charge density.

[0100] In a particularly advantageous manner, the compositions which can be used according to the invention have moreover a dry matter (DM) content greater than 15% and less than 45%, in particular between 18 and 40%.

[0101] The general concept of the present invention is also based on the use of a cationic starchy material having a fixed nitrogen level at most equal to 2% and a weight-average molecular mass of less than 10^7 daltons for the preparation of a starchy composition in accordance with either of the variants described above.

[0102] Advantageously, said cationic starchy material was obtained by treating, before, during and/or after cationization, preferably after cationization, a starchy material with at least one enzyme chosen from the group comprising branching enzymes (EC 2.4.1.18) and cyclodextrin glycosyltransferases or "CGTases" (EC 2.4.1.19), which are thermostable or otherwise.

[0103] The general concept of the present invention is also based on the use of a cationic starchy material having:

[0104] a fixed nitrogen level at most equal to 2%,

[0105] a weight-average molecular mass of less than 10^7 daltons,

[0106] a viscosity, according to the test A, at most equal to 1600 mPa.s, and

[0107] a CDI index greater than 600, for the preparation of a starchy composition useful as paper-making additive other than a standard mass additive or as industrial water treatment additive.

[0108] The applicant company moreover found that, among the starchy compositions described above, which can be used in accordance with the invention, some could also be advantageously used in other fields of application, and in particular in combination with active materials which can be used in mass paper-making such as sizing agents, synthetic polymer(s), optical brightener(s) and/or colorant(s).

[0109] Such combinations may be made in the same mass additive or using separately, simultaneously or otherwise, components of such combinations.

[0110] The weight ratios between synthetic polymer(s) and starchy material(s) during such combinations may be in particular between 1/100 and 100/1 (dry weight/dry weight).

[0111] According to another variant, the compositions according to the invention are characterized by a fixed nitrogen level selected between 0.5 and 1.5%, in particular between 0.6 and 1.5% and a viscosity, determined according to the test A, selected between 10 and 800 mPa.s, in particular between 50 and 700 mPa.s.

[0112] The compositions according to the invention can have a pH which is up to, or even exceeds, the value of 10. However, they preferably have a pH of less than 9, in particular of between 4 and 8.5, and a charge density index CDI greater than 600.

[0113] To the applicant's knowledge, such compositions thus selected constitute novel products whose industrial value results in particular from their capacity to be obtained by simple and inexpensive methods from any starchy materials and to be effectively used and in all safety in all applications, in paper-making or otherwise, commonly involving cationic starchy materials (including mass paper-making and water treatment applications), or even applications such as for example the preparation of compositions containing optical brighteners, not known to use such materials.

[0114] As indicated, said starchy compositions may, at their time of use, already constitute a combination, in any proportions, between the hydrolyzed cationic starch material and one or more other materials and constitute in particular (mass or nonmass) paper-making additives or water treatment additives combining said cationic starchy material and an active material chosen from the group comprising sizing agents, optical brighteners, colorants and synthetic polymers.

[0115] Moreover, and as observed by the applicant, hydrolysis of the cationic starchy material can be perfectly carried out while said material has already been brought into contact with another active material, for example a polyacrylamide, in the additive.

[0116] According to another variant, said starchy compositions may contain only the hydrolyzed cationic starchy material as active material and may be combined, by separate, simultaneous or nonsimultaneous use, with one or more other (mass or nonmass) paper-making additives or water treatment additives containing other active materials such as those cited above.

[0117] By way of example, a starchy composition according to the invention may be used:

[0118] in combination with an active material such as a polyacrylamide in the same additive used at the wet end of the paper-making method,

[0119] in combination with an active material such as an optical brightener or a colorant in the same additive used in mass paper-making or during a paper surfacing or coating operation,

[0120] in combination with a polyacrylamide for the treatment of industrial water, the polyacrylamide being introduced separately, simultaneously or otherwise, of said starchy composition,

[0121] in combination with an optical brightener and/or a colorant, at the wet end of the paper-making process, the materials being introduced separately, simultaneously or otherwise, at the same site of the circuit (for example, at the level of the pulper) or at different sites of the circuit (for example the optical brightener at the level of the pulper and the starchy composition downstream thereof).

[0122] Accordingly, the subject of the present invention is also the use of a starchy composition as described above according to which said starchy composition is combined, simultaneously or otherwise, with at least one other active material, preferably chosen from sizing agents, optical brighteners, colorants and synthetic polymers, in particular polyacrylamides or polyvinylamines.

[0123] The present invention will be described in greater detail with the aid of the examples which follow and which are not at all limiting.

EXAMPLE 1

[0124] A potato starch powder having a total nitrogen level of 1.48% (dry weight/dry weight) and obtained in a dry phase in accordance with the abovementioned patent FR 2,434,821, is mixed and suspended in cold demineralized water so as to obtain a cationic starch milk containing 31% of dry matter ("DM").

[0125] Various samples of said milk are treated with varying levels of α-amylase of the "FUNGAMYL 800 L" type. This enzymatic conversion treatment is carried out in an open tank by increasing the temperature from 20 to 95° C. over 20 minutes and then a plateau of 5 minutes at 95° C., the objective being to be able to obtain cationic starchy compositions having a Brookfield viscosity (measured at 25° C. and at 20 revolutions/minute) of about 300 to 3000 mPa.s and a DM of about 20-22%.

[0126] In practice, the colloidal solutions obtained have a final DM of 21.5%. For each of the solutions obtained, the following characteristics are measured as a function of the level of degrading enzyme used (expressed in %/dry weight of the initial milk):

[0127] Brookfield viscosity at 25° C. and 20 revolutions/minute, expressed in mPa.s, and

[0128] charge density, expressed in microequivalent/gram of dry weight of solution (μeqv/g) and measured on a particle charge detector of the "MUTEK PCD02" type combined with an automated titration device of the "METTLER DL21" type.

[0129] The results obtained are presented below:

Enzyme level (%)	Viscosity (mPa · s)	Charge density (μeqv/g)
0	—	950
0.010	2600	980
0.020	800	970
0.025	380	1006
0.030	320	1022

[0130] Surprisingly, it is noted that in the present case of a cationic starch having a fixed nitrogen level at most equal to 2%, in the present case about 1.5%, and fluidified by the enzymatic route batchwise, the charge density tends to increase significantly while the degree of fluidification increases. The charge density is maximum for the samples having, at a DM of 21.5%, a viscosity of less than 800 mPa.s and in particular less than 380 mPa.s, which would correspond to a viscosity of less than about 700 mPa.s and in particular less than about 330 mPa.s if the DM had been adjusted to 20% according to the test A.

[0131] The applicant company moreover observed that all the compositions based on fluidified cationic starch described above had a remarkable stability during storage, no phenomenon of increase in viscosity or in retrogradation having been observed after 17 days or 4 months of storage at 25° C.

EXAMPLE 2

[0132] In this example, a continuous enzymatic conversion of the cationic potato starch containing 1.48% total nitrogen described in EXAMPLE 1 is carried out. For that, a mixture of "FUNGAMYL 800 L" enzyme and of water is prepared in a proportion of 6.7 milliliters of said enzyme per 100 liters of water. The cationic starch is then fluidified continuously under the following conditions:

[0133] flow rate of water/enzyme mixture: 90 l/h,

[0134] flow rate of cationic starch powder: 60 kg/h, hence the production of a milk containing about 40% of DM,

[0135] reaction time: 30 minutes,

[0136] reaction temperature: 60° C.

[0137] The enzymatic activity is inhibited by passing through an inhibition tube for 1 minute 30 seconds at 140° C. Under these conditions, final DM contents of the order of 26-30% are obtained which are particularly advantageous since they make it possible to obtain viscosities of less than 2000 mPa.s and in particular between 250 and 500 mPa.s.

[0138] In addition, in the particular case of a composition having a final DM of 28%, samples were collected over time and the charge density measured as a function of the viscosity.

[0139] The results obtained are presented below:

Viscosity (mPa · s)	Charge density (μeqv/g)
250	970
300	975
375	980
405	980
450	950
500	965

[0140] It is observed that in the present case of enzymatic fluidification carried out continuously and a viscosity range (250-500 mPa.s at 28% DM) corresponding overall to an average fluidification, there is no correlation between viscosity and charge density.

[0141] In any case, in the context of this example, it appears that compared with the charge density values obtained, viscosities of about 300 to 400 mPa.s are particularly advantageous.

[0142] The dilution of such compositions for the purpose of adjusting the DM thereof to a value of 20% in accordance with the test A described above, then gives viscosities which are preferably less than 150 mPa.s and in particular of the order of 100 to 130 mPa.s.

EXAMPLE 3

[0143] In the context of this example, the cationization of a starch derivative, in the present case of the maltodextrin GLUCIDEX® 2 obtained from waxy corn starch and marketed by the applicant, is carried out. An aqueous solution is prepared containing 50% of DM of this derivative, which solution is heated to a temperature of 70-80° C. 40% of cationic reagent of the TMAEP type as described in the abovementioned patent FR 2.434,821, and 1.5% of sodium hydroxide are then added respectively, these percentages being expressed by dry weight/dry weight of maltodextrin.

[0144] After reaction (5 hours at 50° C.) and neutralization at a pH of 6.7, a starchy composition is obtained which has a DM of 49% and whose viscosity, measured after adjusting the DM to 20% in accordance with the test A, is about 40 mPa.s.

[0145] The cationic starchy material contained in said composition has a fixed nitrogen level of 1.8% (dry weight/dry weight), which indicates a cationic reagent fixing yield of the order of 83% taking into account the total nitrogen level (2.16%) provided by the cationization reagent.

EXAMPLE 4

[0146] In this example, the characteristics of starchy compositions according to the invention as described above are compared in relation to those measured on a cationic starchy composition marketed under the name "RAIFIX 120" for its use as agent for reducing inconvenient materials present in paper-making circuits and designated below "COMPOSITION T". The compositions in accordance with the invention, designated below COMPOSITIONS 1, 2 and 3, result from the preceding EXAMPLES 1, 2 and 3, respectively.

[0147] The characteristics measured relate to the dry matter ("DM" in %), the pH, the total nitrogen level ("TOTAL N" in % dry weight/dry weight), the fixed nitrogen level ("FIXE N" in % dry weight/dry weight), the Brookfield viscosity measured at 20% DM, at 25° C. and 20 rpm according to the test A ("VISCOSITY" in mPa.s), the weight-average molecular mass of the cationic starchy material contained in the composition ("MM" in millions of daltons or 106 d, determined by size exclusion chromatography coupled to a light scattering detector), the charge density ("CD" in μeqv/g) and the CDI index corresponding to the CD/TOTAL N ratio.

[0148] The following results are obtained:

	COMPOSITION			
	T	1	2	3
DM	19.9	21.5	28	49
pH	11.0	5.8	5.8	7.3
TOTAL N	4.6	1.5	1.5	2.2
FIXED N	2.5	1.2	1.2	1.8
VISCOSITY	2600	220	100	40
MM	22.3	1.5	3.0	0.3
CD	2250	1022	980	1300
CDI	489	690	662	722

[0149] The overall result is that the COMPOSITIONS according to the invention, which contain a starchy material which is both significantly less cationized and more fluidified than that contained in the COMPOSITION T according to the prior art, have a high CDI value, considerably higher than that of said COMPOSITION T.

[0150] These high CDI values, greater than 600, or even 650, indicate better fixing of the nitrogen provided by the cationization step and thereby a reduced presence of nitrogenous and saline residues in said COMPOSITIONS 1 to 3.

EXAMPLE 5

[0151] The COMPOSITION 5 (not in accordance with the invention) and the COMPOSITIONS 2 and 3 described above (in accordance with the invention), are tested comparatively as agents for reducing inconvenient substances, anionic or otherwise (collectively designated "pitchs" below), which may be contained in water circuits (and/or retained on equipment), in paper-making or otherwise.

[0152] In the present case, the application medium consists of paper pulp consisting overall, by weight, of about 80% virgin chemical pulps (mixture of leafy and resinous) and 20% of production casse paper. This has a concentration of about 10 g/kg, a conductivity of about 1400 μS/cm, a Zeta potential of −13.4 mV, a pH of 7.7 and a charge density, measured on the supernatant passed through a 140 μm filter, of 85 μeq/l.

[0153] The COMPOSITIONS T, 2 and 3, whose DM has been adjusted to 20%, are introduced into said pulp in a proportion of 0.3% (dry weight/dry weight). The contact time between each of the COMPOSITIONS and the pulp is 5 minutes, with stirring of 1000 rpm.

[0154] A trial is carried out in the absence of any starchy composition. The counting of the "pitchs" is carried out in a standard manner on a THOMAS cell starting with "water under cloth" recovered following the abovementioned treatment and passed through a 30-μm filter.

[0155] The results obtained of Zeta Potential ("POTENTIAL" in mV), charge density ("SCD" in μeq/l) and number of "pitchs" ("PITCHS" in thousands or $10^3/mm^3$ of filtered water under cloth) are presented below:

	POTENTIAL	SCD	PITCHS
WITHOUT COMPOSITION	−13.4	85	49.6
COMPOSITION T	−3.9	19	13.6
COMPOSITION 2	−8.3	62	13.2
COMPOSITION 3	−6.2	48	16

[0156] These results show that COMPOSITIONS according to the invention, although having a relatively low nitrogen level, are perfectly effective as agents for reducing "pitchs". They are overall as effective as the COMPOSITION T, which is nevertheless more difficult to prepare and very significantly more cationized and therefore more expensive and a lot more charged with various residues.

[0157] COMPOSITION 2, in particular, is remarkably suited to this application. The applicant moreover observed that it could be also used as agent for the flocculation of biological and/or mineral sludge obtained from sewage purification plants or as agent for clarifying paper machine water.

EXAMPLE 6

[0158] In the context of this example, the emulsifying properties of COMPOSITION 2 according to the invention, provided in the form of a paste containing 27% of DM, are studied. 13.5 g of the sizing agent "FIBRAN 76" based on alkenylsuccinic anhydride ("ASA") are added to 100 g of said paste, therefore containing in total 27 g of cationic starchy material.

[0159] The sizing composition obtained, which has a weight ratio of starchy material (dry weight)/sizing agent of 2/1, is then subjected to an extensive shearing treatment, namely a 5 minute homogenization at 20,000 revolutions/minute.

[0160] The emulsion thus obtained is then diluted, without stirring, with drilling water in a 1 liter graduated flask so as to obtain an emulsion of "FIBRAN 76" containing 1.35% sizing agent ("EMULSION 1"), a portion of the EMULSION 1 being rediluted, under the same conditions, in order to obtain an emulsion containing 0.3% of sizing agent ("EMULSION 2").

[0161] Observations carried out periodically for a period of 54 hours showed that the EMULSIONS 1 and 2 thus obtained remain perfectly stable and homogeneous.

EXAMPLE 7

[0162] In the context of this example, an additive in accordance with the invention is prepared by treating a cationic starch with a glycogen branching enzyme as described in EXAMPLE 4 of the abovementioned patent WO 00/66633.

[0163] For this purpose, dilute enzyme solution is prepared by providing 150 milliliters of said enzyme in 2 liters of demineralized water, water whose temperature is brought to beforehand and kept at 30° C. and the pH between 7 and 8.

[0164] There is then introduced, by slowly sprinkling, in said dilute enzyme solution, potato starch which is identical to that used in EXAMPLE 1, i.e. having a total nitrogen level of about 1.5% (dry weight/dry weight) and a fixed nitrogen level of about 1.2% (dry weight/dry weight).

[0165] This operation is carried out so that the most regular introduction possible makes it possible to obtain a colloidal solution of said cationic potato starch having a concentration of between 110 and 120 g/l without excessive swelling or energy expenditure necessary during stirring.

[0166] During this preparation phase, the temperature is carefully maintained at 30° C., the pH in the range between 6 and 8 preferably 6.5 to 7.

[0167] Under these conditions, the conversion is continued for 4 hours.

[0168] It is interrupted by deactivation of the enzyme, consisting in maintaining at 95° C. for 15 minutes.

[0169] In practice, the colloidal solution obtained at the end of all these operations has a final DM of 10% and the following characteristics:

Brookfield viscosity:	50 mPa · s (25° C.-20 rpm)
Charge density (CD):	922 μeqv/g
CDI:	615
Weight-average molecular mass (MM): daltons approximately.	3.2×10^6

[0170] It is noted that in the present case of an enzymatic conversion by a branching enzyme, the relatively low viscosity obtained, which would give a value significantly less than 300 mPa.s according to the test A, is compatible with maintaining a relatively high weight-average molecular mass, i.e. greater than 2×10^6 daltons.

[0171] The starchy composition obtained has, as such or after concentration to a DM of about 21.5%, a stability during storage still greater than that observed for the compositions resulting from EXAMPLE 1.

EXAMPLE 8

[0172] In the context of this example, a starchy composition is prepared under the same conditions as those described in EXAMPLE 7, except that:

[0173] 1) The potato starch has a total nitrogen level of about 1.1% (dry weight/dry weight) and a fixed nitrogen level of about 1.0% (dry weight/dry weight).

[0174] 2) The conversion by the branching enzyme is carried out for 45 minutes (instead of 4 hours), and

[0175] 3) The final DM of the colloidal solution obtained is 16.3% (instead of 10%).

[0176] The starchy composition thus obtained has the following characteristics:

Brookfield viscosity:	625 mPa · s
Charge density (CD):	716 μeqv/g
CDI:	650
Weight-average molecular mass (MM): daltons approximately.	2.5×10^6

[0177] It has remarkable stability during storage.

[0178] In addition, the applicant company has verified that said composition could be perfectly suitable as agent for reducing inconvenient materials present in paper-making circuits since, under the test conditions described in EXAMPLE 5 above, said composition made it possible to obtain effects comparable to those observed with the COMPOSITIONS 2 OR 3, in this case a Zeta potential of −6.4 mV, a charge density value (SCD) of 65 μeq/l and a number of "pitchs" of 16.4×10^3/mm^3 of filtered water under cloth.

EXAMPLE 9

[0179] In the context of this example, the value of a starchy composition in accordance with the invention is studied in the context of the combination with an optical brightener and, optionally other colorants.

[0180] The starchy composition in accordance with the invention was obtained by enzymatic conversion, by alpha-amylase, of a cationic potato starch having a total nitrogen level of about 1.65% and a fixed nitrogen level of about 1.5%.

[0181] It is provided in the form of a paste whose principal characteristics are the following:

Dry matter (DM):	27.9%
Brookfield viscosity:	450 mPa.s (25° C. - 20 rpm)
Charge density:	1056 μeqv/g
CDI:	640 approximately

[0182] In the present case, the active materials are introduced into the mass of a paper pulp consisting by weight of approximately:

[0183] 20% of resinous kraft pulp

[0184] 60% of leafy kraft pulp, and

[0185] 20% of casse paper

[0186] Before introducing said pulp into a disintegrating device, the following are successively introduced into the water for filling said device:

[0187] a) either a cationic starchy composition described above or a cationic polyacrylamide, this being in a quantity equivalent to the DM of said starchy composition, and then,

[0188] b) an optical brightener, this being in a quantity equal to about 5 times the quantity of cationic product used in a), and then, optionally, a mixture of colorants, this being in a quantity equal to about 2.5 times the quantity of cationic product used in a).

[0189] After introducing the pulp and disintegrating it for 30 minutes, sheets are produced having a substance of about 80 g/m^2 with the aid of the material "TECHPAP".

[0190] Measurements of whiteness and of fluorescence are essentially carried out on them.

[0191] The results obtained showed overall that the starchy composition according to the invention, containing an enzymatically converted cationic starchy material, makes it possible to have an efficiency of the optical brightener at least as high as, generally greater than, that obtained with the synthetic cationic polymer, this being both in the presence and in the absence of coloring matter.

EXAMPLE 10

[0192] In the context of this example, the value of starchy compositions, in accordance with the present invention or not, is studied in the field of the treatment of water, this being in the context of combinations with a synthetic coagulant, in this case the cationic polyacrylamide "PERFORM PA 9430" marketed by HERCULES.

[0193] For the TRIALS A, B and C, said polyacrylamide is tested in combination with a starchy paste based respectively:

[0194] TRIAL A: on a cationic potato starch containing about 0.64% of fixed nitrogen (dry weight/dry weight), nonhydrolyzed and therefore not in accordance with the present invention,

[0195] TRIAL B: on a cationic potato starch containing about 1.5% of fixed nitrogen (dry weight/dry weight), hydrolyzed with alpha-amylase in accordance with the invention, or

[0196] TRIAL C: on a cationic potato starch (fixed nitrogen: about 1.5% as dry weight/dry weight), hydrolyzed with branching enzyme in accordance with the invention.

[0197] In addition, a control trial ("TRIAL T") is carried out for which said polyacrylamide is not combined with a starchy composition.

[0198] For all these trials, a paper-making effluent is treated which has a suspended matter level of the order of 1.6 g/l.

[0199] The effluent sample collected is immediately placed under stirring. The following succession of steps are then carried out:

[0200] at t=1 minute: introduction (TRIALS A to C) or otherwise (TRIAL T) of the starchy composition into the stirred effluent, this being with an introduction rate of 0.03°/°° (dry weight/dry weight),

[0201] at t=6 minutes: introduction of the synthetic coagulant (TRIALS T and A to C), this being at the rate of 0.001°/°°, expressed as commercial weight/dry weight of the effluent,

[0202] at t=7 minutes: termination of stirring,

[0203] from t=7 minutes to t=9 minutes: observation of decantation,

[0204] from t=12 minutes: measurements of the dry matter content of the supernatant ("DMS" in g/l) and the optical density of the supernatant ("OD").

[0205] The results below are obtained for the TRIALS T and A, not in accordance with the invention and TRIALS B and C, in accordance with the invention.

	DMS g/l	OD
TRIAL T	0.335	4.6
TRIAL A	0.304	5.0
TRIAL B	0.244	4.4
TRIAL C	0.216	4.3

[0206] These results show overall that the starchy compositions in accordance with the invention can be advantageously used in the treatment of water, in particular in combination with a synthetic polymer such as a cationic polyacrylamide (cf. TRIALS B and C).

[0207] These starchy compositions make it possible to very significantly improve the purification of effluent by reducing the dry matter content and the optical density of the supernatant, this being to a much greater extent than can be obtained with a starchy composition not in accordance with the invention (cf. TRIAL A).

[0208] The starchy composition tested in TRIAL C, based on cationic starchy material converted by a branching enzyme, appears to be particularly efficient in combination with a cationic polyacrylamide.

EXAMPLE 11

[0209] In the context of this example, a hydrolyzed cationic material in accordance with the invention and a cationic polyacrylamide such as the product "PRAESTOL 853 BC" marketed in powdered form by STOCKHAUSEN are combined in the same additive, which can be used in (mass or nonmass) paper-making or in the treatment of water.

[0210] Such a combination can be advantageously made, as in the present case, by bringing the starchy material and the synthetic material into contact with each other immediately before the step of conversion aimed at hydrolyzing the cationic starchy material.

[0211] A starch milk containing 30% of DM is prepared from the same cationic potato starch powder as that used in EXAMPLE 1. 5% of said cationic polyacrylamide are then added to the suspension, this percentage being expressed by weight of commercial polyacrylamide over the dry starch weight.

[0212] 0.15°/°° of alpha-amylase of the "FUNGAMYL 800 L" type, expressed by weight of commercial product relative to the starch dry weight, is then added.

[0213] The enzymatic conversion treatment is then carried out in an open tank by increasing the temperature from 20 to 95° C. over 20 minutes with live steam and then a plateau of 5 minutes at 95° C. in order to inhibit the enzyme.

[0214] The DM of the composition obtained is then adjusted to a value of about 22%.

[0215] The starchy composition obtained, combining hydrolyzed cationic starchy material and cationic polyacrylamide, has the following main characteristics:

DM:	22.2%
Brookfield viscosity:	1500 mPa · s (25° C. - 20 rpm)
Charge density:	1040 μeqv/g

[0216] It is observed that the viscosity of this composition is increased compared with that obtained, in the absence of a synthetic polymer, with 0.15°/° of alpha-amylase according to EXAMPLE 1.

[0217] However, this viscosity is in conformity with the objective set, namely at most equal to 1600 mPa.s (according to the test A).

[0218] In addition, observations made by the applicant show that this composition remains stable, after a storage of 25 days at 25° C., and that the hydrolyzed cationic starchy material which it contains is perfectly solubilized.

1. The use, as paper-making additive other than a standard mass additive or as water treatment additive, of a starchy composition containing at least one cationic starchy material, characterized in that said composition has:

a fixed nitrogen level at most equal to 2%, preferably between 0.1 and 1.9%, these percentages being expressed by dry weight relative to the dry weight of the composition, and

a viscosity, determined according to a test A, at most equal to 1600 mPa.s, preferably between 5 and 1500 mPa.s.

2. The use as claimed in claim 1, characterized in that the starchy composition has a fixed nitrogen level of between 0.2 and 1.5%.

3. The use as claimed in either of claims **1** and **2**, characterized in that the cationic starchy material has a weight-average molecular mass of less than 10^7 daltons, preferably less than 5×10^6 daltons.

4. The use as claimed in claim 3, characterized in that the cationic starchy material has a weight-average molecular mass of between 10^4 and 4×10^6 daltons.

5. The use as claimed in any one of claims 1 to 4, characterized in that the starchy composition has a charge density index CDI greater than 600, preferably greater than 650.

6. The use as claimed in claim 5, characterized in that the starchy composition has a CDI value of between 660 and 800.

7. The use as claimed in any one of claims 1 to 6, characterized in that the starchy composition has a pH of less than 9, preferably of between 4 and 8.5.

8. The use, as claimed in any one of claims 1 to 7, characterized in that the starchy composition has:

a fixed nitrogen level of between 0.4 and 1.5%, and

a viscosity, determined according to a test A, of between 10 and 800 mPa.s.

9. The use as claimed in claim 8, characterized in that the starchy composition has:

a fixed nitrogen level of between 0.5 and 1.5%, and

a viscosity of between 50 and 700 mPa.s.

10. The use as claimed in any one of claims 1 to 9, characterized in that the starchy composition has a dry matter content greater than 15% and less than 45%, preferably between 18 and 40%.

11. The use of a cationic starchy material having a fixed nitrogen level at most equal to 2% and a weight-average molecular mass of less than 10^7 daltons for the preparation of a starchy composition used as claimed in any one of claims 1 to 10.

12. The use as claimed in claim 11, characterized in that the cationic starchy material was obtained by treating a starchy material, before, during and/or after its cationization, preferably after its cationization, with at least one enzyme chosen from the group comprising branching enzymes (EC 2.4.1.18) and cyclodextrin glycosyltransferases (EC 2.4.1.19), which are thermostable or otherwise.

13. The use of a starchy composition as claimed in any one of claims 1 to 10 or prepared as claimed in either of claims **11** and **12**, as agent for reducing inconvenient substances contained in water circuits and/or retained on process equipment, for paper-making or otherwise, as additive in the preparation of sizing agent compositions used in paper-making, in particular as agent for protecting said agents, as additive in the preparation of compositions for creping, surfacing or coating paper, or as additive in the preparation of compositions containing optical brighteners, colorants and/or synthetic polymers, in particular polyacrylamides or polyvinylamines.

14. A starchy composition containing at least one cationic starchy material characterized in that said composition has:

a fixed nitrogen level of between 0.5 and 1.5%, these percentages being expressed by dry weight relative to the dry weight of the composition, and

a viscosity, determined according to a test A, of between 10 and 800 mPa.s.

15. The starchy composition as claimed in claim 14, characterized in that it has:

a fixed nitrogen level of between 0.6 and 1.5%, and

a viscosity of between 50 and 700 mPa.s.

16. The starchy composition as claimed in either of claims **14** and **15**, characterized in that it has:

a pH of less than 9, preferably of between 4 and 8.5, and

a charge density index CDI greater than 600.

17. The use of a composition as claimed in any one of claims 14 to 16, as paper-making additive or as industrial water treatment additive.

18. The use as claimed in claim 17, characterized in that the starchy composition is combined, simultaneously or otherwise, with at least one other active material, preferably chosen from sizing agents, optical brighteners, colorants and synthetic polymers, in particular polyacrylamides or polyvinylamines.

19. The use as claimed in claim 18, characterized in that the weight ratio synthetic polymer(s)/cationic starchy material(s) is between 1/100 and 100/1, said ratios being expressed as dry weights of synthetic polymer(s) on the one hand and of cationic starchy material(s) on the other hand.

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