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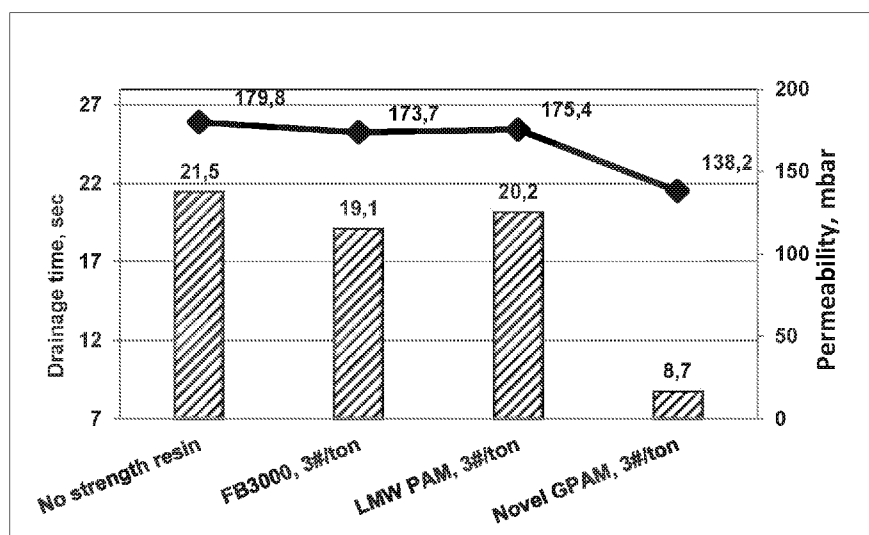


Fig. 1

(57) Abstract: The present disclosure relates to an improved process for manufacturing paper product or the like. The process comprises incorporating a drainage system into the fibre suspension, which drainage system comprises inorganic siliceous microparticles and a structurally modified, water-soluble glyoxylated polyacrylamide having an intrinsic viscosity at least 0.5 dl/g, preferably at least 0.7 dl/g and more preferably at least 1.0 dl/g, as determined by gel permeation chromatography (GPC).



DRAINAGE SYSTEM AND PROCESS FOR MANUFACTURING PAPER PRODUCT OR THE LIKE

Field of the invention

5

The present invention relates to a process for manufacturing paper product or the like according to the preambles of the independent claims presented below, in which process a drainage system is incorporated into a fibre suspension.

10

Background of the invention

The systems of drainage and retention aids comprising cationic high molecular weight retention polymers (polymer molecular weight range in 10-
15 million Dalton) and silica based microparticles are one of the most commonly used drainage systems on paper machines. These drainage systems are introduced into the fibre suspension in order to facilitate drainage and increase adsorption of fine particles onto the cellulose fibres so that they are retained with the fibres.

20

Due to the increased environmental awareness and regulations, papermaking processes have become more and more closed using less fresh water, resulting in increased conductivity or total ionic strength, i.e. salt concentration, in the fibre suspension. Concurrently, the recycled fibre
25 content has increased as a fibre source in the papermaking. Recycled fibre materials may introduce significant levels of detrimental substances to the papermaking process. This may include ash originating from coating pigments and fillers, starch, sizing agents, dissolved and colloidal substances. These substances carried over to the papermaking process may
30 further increase the overall colloidal load and conductivity of the fibre suspension, accumulating in the process water circuit. These materials may cause plugging and deposits on the equipment and produced paper.

The efficiency of the conventional drainage and retention aids usually is
35 deteriorated in the presence of the detrimental substances or high conductivities. The loss of polymer performance leads to decreases in drainage efficiency, retention of fibre and fibre fines, and press dewatering,

which increases the drying demand of the paper, requiring an increase in steam consumption in the dryer section. Steam availability is limited in the paper production facility. Consequently, drying demand of the paperboard is often a rate limiting step with respect to productivity rates. The conventional
5 high molecular weight retention polymers cannot be used in increasing dosages because they have the adverse effect of over flocculating the sheet due to the extremely high molecular weight and resulting in uneven formation of final paper.

10 Thus, there is a constant need for chemical additive systems providing improved drainage to a papermaking process, and preferably tolerating elevated conductivity without substantial performance loss.

15 **Summary of the Invention**

It is an object of the present invention to reduce or even eliminate the above-mentioned disadvantages existing in prior art.

20 One object of the present invention is to provide a process for making a paper product or the like with improved drainage, and optionally improved retention. More detailed, the object of the present invention is to provide a use of a structurally modified, water-soluble glyoxylated polyacrylamide in a papermaking process with inorganic siliceous microparticles for improving
25 drainage, and optionally retention.

Another object of the present invention is to provide a process for manufacturing a paper product or the like with improved drainage, and optionally retention, when using fibre suspension comprising recycled fibre
30 material.

The object of the present invention is also to provide a process for manufacturing a paper product or the like with improved drainage, and optionally retention, when using fibre suspension having elevated
35 conductivity.

Yet another object of the present invention is to provide an improved paper product.

5 These objects are attained with the invention having the characteristics presented below in the characterizing parts of the independent claims.

Some preferable embodiments of the invention are presented in the dependent claims. The features recited in the dependent claims are freely combinable with each other unless otherwise explicitly stated. More
10 precisely, the embodiments of the present disclosure described in this specification may be combined, in whole or in part, with each other. Even several of the embodiments may be combined, in whole or in part, together to form a further embodiment of the present disclosure. Further, the particular features or characteristics described in this specification may be combined in
15 any suitable manner in one or more embodiments. Thus, the particular features or characteristics illustrated or described in connection with various embodiments may be combined, in whole or in part, with the features or characteristics of one or more other embodiments without limitation. Such modifications and variations are intended to be included within the scope of
20 the present disclosure. A process, a drainage system, a use or a paper product, to which the present disclosure is related, may comprise at least one of the embodiments of the present disclosure described in this specification. The embodiments and advantages mentioned in this text relate, where applicable, both to the process, the drainage system as well as to the uses
25 according to the invention, even though it is not always specifically mentioned.

Typical process according to the invention for manufacturing paper product or the like comprises

- 30 - providing a fibre suspension,
- incorporating a drainage system into the fibre suspension, which drainage system comprises inorganic siliceous microparticles and a structurally modified, water-soluble glyoxylated polyacrylamide having an intrinsic viscosity at least 0.5 dl/g, preferably at least 0.7 dl/g and more preferably at
35 least 1.0 dl/g, as determined by gel permeation chromatography (GPC), and
- forming the fibre suspension into a fibrous web.

Typical drainage system according to the invention for improving drainage in manufacturing of paper product or the like comprises inorganic siliceous microparticles and a structurally modified, water-soluble glyoxylated polyacrylamide having an intrinsic viscosity at least 0.5 dl/g, preferably at least 0.7 dl/g and more preferably at least 1.0 dl/g, as determined by gel permeation chromatography (GPC).

Typical paper product comprises the drainage system according to invention, or it is manufactured by the process according to the invention.

According to one preferred embodiment of the invention, the structurally modified, water-soluble glyoxylated polyacrylamide is a structurally modified, water-soluble glyoxylated cationic polyacrylamide.

It has been surprisingly found that the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention, when used in combination with inorganic siliceous microparticles, provide drainage improvements beyond the standard additive program of high molecular weight retention polymer and silica sol, even if the standard additive program is boosted with a conventional GPAM polymer. Especially, when the structurally modified, water-soluble glyoxylated polyacrylamide is a glyoxylated cationic polyacrylamide according to the invention, the combination with inorganic siliceous microparticles provides exceptional drainage improvements.

The structurally modified, water-soluble glyoxylated polyacrylamide according to the invention is preferably an aqueous composition obtainable by

- (i) providing a polyacrylamide having a standard viscosity of at least about 1 cP, measured at 0.1 weight-% polymer concentration in 0.1 M NaCl, at 25 °C and pH 8.0 – 8.5, using Brookfield DVII T viscometer, in an aqueous medium,
- (ii) incorporating in said aqueous medium a degradation agent capable of reducing the standard viscosity of the polyacrylamide in the aqueous environment by cleaving a backbone of the polyacrylamide, and
- (iii) cross-linking the polyacrylamide subjected to cleaving by introducing glyoxal to said aqueous medium for obtaining an aqueous composition of the structurally modified, water-soluble glyoxylated polyacrylamide.

The structurally modified, water-soluble glyoxylated polyacrylamide according to the invention is preferably made from dry polyacrylamide backbones by the method disclosed above, when it may achieve higher molecular weight than the conventional GPAM polymers, typically manufactured by glyoxylating low molecular weight cationic polyacrylamide based polymers obtained by solution polymerization. Because of their high molecular weight competencies and/or the novel network structure, the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention has been found to yield stronger synergistic interaction with inorganic siliceous microparticles used as drainage aids, compared to the conventional GPAMs. Especially, a pronounced synergistic interaction has been found with inorganic siliceous microparticles having high specific surface area (SSA) and high structure in terms of low S-value, such as silica sols.

Typically a structurally modified, water-soluble glyoxylated polyacrylamide according to the invention has an intrinsic viscosity (IV) at least 0.5 dl/g, preferably at least 0.7 dl/g and more preferably at least 1.0 dl/g, as determined by gel permeation chromatography (GPC); said structurally modified, water-soluble glyoxylated polyacrylamide has preferably been obtained by the method described in this application. The GPC system and measurement conditions are described more specifically in Example 1.

In a typical embodiment of the invention, a polydispersity index (M_w/M_n) of a structurally modified water-soluble glyoxylated polyacrylamide according to the invention is < 5.0 , preferably < 4.0 and more preferably < 3.5 . A typical mass average molar mass (M_w) of a structurally modified, water-soluble glyoxylated polyacrylamide according to the invention is at least 0.5 Mg/mol, preferably at least 0.7 Mg/mol and more preferably at least 1.0 Mg/mol. A number average molar mass (M_n) of a structurally modified, water-soluble glyoxylated polyacrylamide according to a typical embodiment of the invention is at least 2.8×10^5 g/mol, preferably at least 3.0×10^5 g/mol and more preferably at least 3.2×10^5 g/mol. M_w , M_n and polydispersity index (M_w/M_n) are determined by GPC. The GPC system and measurement conditions are described more detailed in Example 1.

It is believed that the high molecular weight in combination with the novel structure of the structurally modified water-soluble polymer according to the

invention facilitates strong interaction with the inorganic siliceous microparticles yet without over-flocculating the papermaking system in ever increasing polymer dosage. The opportunity to increase dosage without over-flocculation is especially advantageous when the fibre suspension contains
5 detrimental substances and/or high conductivities.

Especially, exceptional drainage improvement for fibre suspensions comprising recycled fiber materials has been discovered when the structurally modified, water-soluble glyoxylated polyacrylamide according to
10 the invention is used with inorganic siliceous microparticles. Therefore, the benefit of the invention is to improve the drainage of fibre suspensions comprising recycled fibre material and thus comprising even high amounts of detrimental substances such as dissolved solids and/or high ash content.

15 Similarly, an exceptional drainage improvement can be expected for fibre suspensions comprising high filler content when the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention is used with inorganic siliceous microparticles. Therefore, the benefit of the invention is to improve the drainage of fibre suspensions comprising high filler content.

20 Additionally, exceptional drainage improvement for fibre suspensions having elevated conductivity has been discovered when the structurally modified water-soluble glyoxylated polyacrylamide according to the invention is used with inorganic siliceous microparticles. Therefore, the benefit of the invention
25 is to improve the drainage of fibre suspensions having elevated conductivity, especially in paper or board mills having closed processes using less fresh water.

30 All paper products and the like may benefit from the drainage system according to the present invention, especially recycled paperboard, tissue/towel, and printing and writing papers, just to name a few.

This invention is for use of structurally modified, water-soluble glyoxylated polyacrylamide as boosters for inorganic siliceous microparticle drainage aids
35 and as paper strength resins.

Brief description of the figures

Figures 1 to 3 show the results of dynamic drainage analyser (DDA) studies according to Examples 2 to 4.

5

Detailed description of the invention

Standard viscosity is used herein to reflect or indicate the molecular weights for polymers having molecular weights more than 1 million Dalton. Standard
10 viscosity as used herein is determined with a Brookfield DVII T viscometer. A 0.2 weight-% water solution of a polymer is diluted to 0.1 weight-% concentration with 11.7 weight-% NaCl solution to make a 50:50 solution of the polymer and 11.7 weight-% NaCl in a 250 mL beaker, i.e. 0.1 weight-% polymer concentration in 1 M NaCl. Then, pH of the 0.15 weight-% salt dilute
15 polymer solution is adjusted to pH 8.0 - 8.5 by dilute NaOH solution or H₂SO₄ solution before the viscosity measurement. 19 ml of solution is taken using a graduated cylinder, and slowly poured into the Brookfield SV chamber and the temperature of the SV solution in the chamber is adjusted to 25 °C. The viscosity of 0.1 weight-% solution is measured at 25 °C, using spindle #00,
20 the spindle speed being 60 RPM. The unit of SV is centipoise (cP).

Bulk viscosity is used herein to indicate the viscosity of an aqueous solution of a polymer in the prevailing solids content. As used herein, bulk viscosity is determined with a Brookfield DVII T viscometer at 25 °C. The unit of bulk
25 viscosity is equally centipoise (cP).

A backbone of a polyacrylamide refers in this disclosure to the main chain of the polyacrylamide which is a result of the (co)polymerisation reaction of acrylamide, and optionally any cationic, anionic or non-ionic monomers
30 copolymerisable with acrylamide. Anionic monomers are monomers possessing a negative net charge, cationic monomers are monomers possessing a positive net charge, and non-ionic monomers are monomers possessing a net charge of 0. The main chain is substantially linear chain to which all other chains may be regarded as pendant.

35

As used herein, the term "water-soluble" is understood so that the glyoxalated polyacrylamide is miscible with water. When mixed with an

excess of water, the glyoxalated polyacrylamide is preferably fully dissolved and the obtained glyoxalated polyacrylamide solution is preferably essentially free from discrete polymer particles or granules. Excess of water means that the obtained glyoxalated polyacrylamide solution is not a saturated solution.

5

As used herein, the term “degradation agent” refers to any compound or mixture of compounds which is capable of reducing the standard viscosity of a polyacrylamide when in an aqueous environment by cleaving the backbone of the polyacrylamide, i.e. the main chain of the acrylamide polymer, into
10 fragments. The effect of the degradation agent and the cleavage of the polymer backbone can be seen in the decreasing viscosity of the aqueous medium comprising the polyacrylamide.

As used herein, the term “cross-linking” refers to covalently linking two target
15 groups present in the polyacrylamide and/or in the fragments thereof, which fragments are resulted from the cleaving of the polyacrylamide backbone. Herein, glyoxal is a preferred cross-linking agent for covalently linking cleaved fragments of the acrylamide polymer to other said fragments and/or to the backbone of the acrylamide polymer.

20

According to one embodiment of the invention, the present invention provides a process for manufacturing paper product or the like, wherein a drainage system is incorporated into a fibre suspension, which drainage system comprises inorganic siliceous microparticles and a structurally modified,
25 water-soluble glyoxylated polyacrylamide having an intrinsic viscosity at least 0.5 dl/g, preferably at least 0.7 dl/g and more preferably at least 1.0 dl/g, as determined by GPC. Preferably, the structurally modified, water-soluble glyoxylated polyacrylamide is obtained by

- (i) providing a polyacrylamide having a standard viscosity of at least about 1
30 cP, measured at 0.1 weight-% polymer concentration in 0.1 M NaCl, at 25 °C and pH 8.0 – 8.5, using Brookfield DVII T viscometer, in an aqueous medium,
- (ii) incorporating in said aqueous medium a degradation agent capable of
35 reducing the standard viscosity of the polyacrylamide in the aqueous environment by cleaving a backbone of the polyacrylamide, and

(iii) cross-linking the polyacrylamide subjected to cleaving by introducing glyoxal to said aqueous medium for obtaining an aqueous solution of the structurally modified, water-soluble glyoxylated polyacrylamide.

- 5 When a structurally modified, water-soluble glyoxylated polyacrylamide is prepared by the method disclosed above, the glyoxylated polyacrylamide may be obtained in the form of an aqueous, non-gelled composition surprisingly expressing a synergistic interaction with inorganic siliceous microparticles providing an exceptional drainage improvement. Furthermore,
10 the structurally modified, water-soluble glyoxylated polyacrylamide may provide an excellent strength response.

In one embodiment of the invention, the polyacrylamide used in the method for preparing a structurally modified water-soluble glyoxylated polyacrylamide
15 has a standard viscosity of at least 1.2 cP, preferably at least 1.5 cP, more preferably at least 2.0 cP, measured at 0.1 weight-% polymer concentration in 0.1 M NaCl, at 25 °C, pH 8.0-8.5, using Brookfield DVII T viscometer. Higher standard viscosity of the polyacrylamide corresponds to higher molecular weight. High molecular weight polymers are available in higher
20 solids content, even as dry powders. As the polyacrylamide backbone being subjected to degradation agent has higher molecular weight, also the structurally modified water-soluble polyacrylamide obtained after cross-linking with glyoxal may have higher molecular weight. Typically, the polyacrylamide has a molecular weight of at least 2 million Dalton, preferably
25 at least 5 million Dalton or even more preferably at least 10 million Dalton. According to an embodiment of the invention the polyacrylamide has a molecular weight in the range of 10 to 20 million Dalton, or in the range of 10 to 15 million Dalton. Preferably, the polyacrylamide is a dry polymer which allows for improved logistics both cost and product robustness for
30 challenging climate conditions.

In the preparing of a structurally modified, water-soluble glyoxylated polyacrylamide of the drainage system, the degradation agent and the cross-linking agent may be pre-mixed together before addition, or they may be
35 added separately such as sequentially, the degradation agent being added before glyoxal as the cross-linking agent. The additions of the degradation agent and the glyoxal may also overlap, in which case the addition of the

degradation agent may continue when the glyoxal addition is started. In this way the degradation agent starts breaking of the polyacrylamide backbone earlier than the cross-linking starts, but breaking of the backbone into fragments still continue at same time with cross-linking reaction. In one
5 embodiment the polyacrylamide and the degradation agent are introduced into the aqueous composition first, and the cross-linking agent, preferably glyoxal, is introduced thereto subsequently. Advantageously, the degradation agent starts breaking of the polyacrylamide backbone before the cross-linking starts. The degradation agent continues breaking of the
10 polyacrylamide backbone in parallel with cross-linking e.g. by the glyoxylation, until all of the degrading power of the degradation agent has been consumed or quenched. Cross-linking reaction, on the other hand, may be an equilibrium reaction, as is the case for e.g. glyoxylation. Thus, the bulk viscosity of the aqueous composition of the cross-linking and degrading
15 polyacrylamide evolves until the degrading power of the degradation agent has been consumed or quenched and the cross-linking, preferably glyoxylation, reaction has reached an equilibrium.

In one embodiment of preparing a structurally modified, water-soluble
20 glyoxylated polyacrylamide, the polyacrylamide and the degradation agent is dissolved in the aqueous medium simultaneously as a dry mixture. The dry mixture may be provided by mixing dry polyacrylamide and dry degradation agent. This embodiment has the additional utility that the dry mixture has good storage stability, is easily and cost-efficiently transported to the site of
25 use, and the cleaving of the backbone of the polyacrylamide does not start before the dry mixture is brought into an aqueous environment. In one embodiment the degradation agent is mixed into a further aqueous medium and then combined with the polyacrylamide in the aqueous medium. In one embodiment dry polyacrylamide is dissolved in an aqueous solution of the
30 degradation agent.

In one embodiment of preparing a structurally modified, water-soluble glyoxylated polyacrylamide, step (iii) of the method is initiated after all degradation agent has been incorporated to the aqueous medium in step (ii)
35 of the method, i.e. cross-linking of the polyacrylamide subjected to cleaving is initiated to the aqueous medium only after all degradation agent has been incorporated to the aqueous medium. In another embodiment at least step

(iii) of the method, i.e. crosslinking of the polyacrylamide subjected to cleaving, is conducted on site of the use of the aqueous composition of the structurally modified, water-soluble glyoxylated polyacrylamide.

5 The degradation agent used in the method for preparing a structurally modified, water-soluble glyoxylated polyacrylamide may be any compound or mixture of compounds capable of breaking, i.e. cleaving the backbone of the polyacrylamide in an aqueous environment into smaller polymeric fragments. This has the effect of reducing the standard viscosity of the polyacrylamide,
10 and the effect of reducing the bulk viscosity of an aqueous composition comprising the polyacrylamide. In other words, the degradation agent may be any compound or mixture of compounds capable of reducing the standard viscosity of the polyacrylamide by cleaving the backbone of the polyacrylamide into polymeric fragments thereof.

15 The degradation agent used in the method for preparing a structurally modified, water-soluble glyoxylated polyacrylamide may be selected from compounds or mixtures of compounds capable of reducing the standard viscosity of the polyacrylamide by at least 5 %, advantageously by at least 10
20 %. Mere hydrolysis of side groups of e.g. an acrylamide based copolymer does not cause sufficient reduction of viscosity. In one embodiment the degradation agent is selected from oxidizing degradation agents, reducing degradation agents, or any combinations thereof. Preferably, the degradation agent is a reducing degradation agent.

25 In one embodiment the oxidizing degradation agent is selected from the group consisting of sodium percarbonate, sodium hypochlorite, sodium persulfate, potassium persulfate, ammonium persulfate, hydrogen peroxide, sodium perborate, or any combinations thereof. In one embodiment the
30 reducing degradation agent is selected from the group consisting of an iron compound, tin(II) chloride, sodium borohydride (NaBH_4), sodium dithionite, or any combinations thereof. Reducing degradation agents may provide faster degradation than oxidizing agents. The degradation agent may also be an enzymatic degradation agent, such as an oxidase. In an exemplary
35 embodiment the degradation agent is selected from the group consisting of an iron compound, sodium borohydride (NaBH_4), sodium dithionite, sodium percarbonate, sodium persulfate, potassium persulfate, ammonium

persulfate, hydrogen peroxide, sodium perborate, to avoid incorporating chlorides.

5 In a preferred embodiment, the degradation agent comprises an iron compound. This compound is advantageously a ferrous compound such as a ferrous salt or a ferric compound such as a ferric salt, these being available in dry powder form. Iron compounds are generally environmentally friendly compounds. The term ferrous is used according to its customary meaning to indicate a divalent iron compound (+2 oxidation state or Fe(II)). The term
10 ferric is used according to its customary meaning to indicate a trivalent iron compound (+3 oxidation state or Fe(III)). In an exemplary embodiment the ferrous salt comprises an organic anion, an inorganic anion, or a mixture thereof. In an advantageous embodiment, the ferrous salt is ferrous citrate, ferrous chloride, ferrous bromide, ferrous fluoride, ferrous sulfate, ammonium
15 iron sulfate or any combinations thereof. In one embodiment, the iron-containing degradation agent comprises ferrous sulfate. In an exemplary embodiment, the ferric salt comprises an organic anion, an inorganic anion, or a mixture thereof. In exemplary embodiments, the ferric salt is ferric citrate, ferric chloride, ferric bromide, ferric fluoride, ferric sulfate, and any
20 combinations thereof.

The most advantageous polymer degradation agent for use in the present disclosure is iron(II)sulfate. Iron sulfate, in particular ferrous sulfate, is able to dissolve and degrade at ambient pulp suspension conditions whereas the
25 other degradation agents require elevated temperature to achieve the same polymer degradation effectiveness. Together with the ferrous or ferric iron compound another polymer degradation agent may be used, such agent being advantageously selected from the group consisting of persulfates, peroxides, sodium chlorite, tin(II)chloride and percarbonates.

30 In one embodiment the amount of the degradation agent varies from 0.5 to 15 weight-% of the polyacrylamide, preferably 2.5 to 10 weight-%, calculated as dry. In case the degradation agent contains crystal water, the expression calculated as dry includes the crystal water. In this range the degradation of
35 the polymer backbone proceeds adequately, yet controllably, so as to avoid the degradation from proceeding too extensively thereby causing too low

molecular weight. The amount of the degradation agent is expressed excluding the potential bound water.

5 In one embodiment the polyfunctional cross-linking agent is a dialdehyde cross-linking agent providing aldehyde functionality to the cross-linked polyacrylamide, rendering the polyacrylamide cellulose-reactive. Preferably the cross-linking agent is a glyoxal, which is a common commercially available dialdehyde. Glyoxal may provide faster cross-linking reaction compared e.g. to dialdehydes having higher chain length / number of carbon
10 atoms.

The cross-linking reaction of preparing a structurally modified, water-soluble glyoxylated polyacrylamide, such as glyoxylation itself in the present disclosure may be any known or obvious glyoxalation sequence. An example
15 of a representative disclosure for carrying out glyoxylation is presented in US 8,435,382. Generally, conventional GPAM is prepared by reacting a cationic polyacrylamide backbone, with glyoxal in a slightly alkaline aqueous solution, pH from about 7 to 8, and by stabilizing under acidic conditions pH from about 3 to 6.

20 In one embodiment the amount of glyoxal is from 5 to 80 weight-%, preferably from 8 to 60 weight-%, more preferably from 8 to 30 weight-% of the acrylamide polymer, calculated as dry. Amounts above 80 weight-% may provide extremely high reaction speed. On the other hand amounts below 5
25 weight-% may provide unreasonably slow reaction rate. Amounts up to 60 weight-%, especially up to 30 weight-%, may provide reaction speed that is convenient to control. In one embodiment, glyoxal to acrylamide unit molar ratio is at least 0.4. Advantageously, glyoxal to acrylamide unit molar ratio is from 0.4 to 0.70.

30 In one embodiment the polyacrylamide used in said method for preparing a structurally modified, water-soluble polymer is a copolymer originating from at least 50 mol-% of acrylamide monomers. Dialdehyde cross-linking agents such as glyoxal may react with the amide group of the acrylamide. Thus the
35 acrylamide monomer level of at least 50 mol-% provides good cross-linking rate and level of cross-linking thereby increasing the molecular weight of the

cross-linked polymer, and thus the strength performance thereof in papermaking.

5 In one embodiment of a structurally modified, water-soluble glyoxylated polyacrylamide, the polyacrylamide is a cationic polyacrylamide, i.e. a (co)polymer having net cationic charge. In one embodiment the polyacrylamide is an anionic polyacrylamide, i.e. a (co)polymer having net anionic charge. In one embodiment the polyacrylamide is a nonionic polyacrylamide, i.e. an acrylamide (co)polymer, such as homopolymer, not
10 having charge. Net cationic charge is preferred as cationic charge binds efficiently to anionic fibres and anionic particles in the fibre suspension. In certain other papermaking situations anionic net charge may be preferred, for example when interaction with other, cationic chemicals is desired. In certain other papermaking situations non-ionicity may be preferred, for example
15 when presence of charges would interfere other interactions taking place, or when the nonionic polymer comprises hydrophobic monomers as the interacting groups.

In one embodiment of a structurally modified, water-soluble glyoxylated
20 polyacrylamide the polyacrylamide is a copolymer comprising units originating from acrylamide and cationic monomers, wherein cationic monomers are preferably selected from the group consisting of 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-dimethylaminoethyl methacrylate
25 (MADAM), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC), and diallyldimethylammonium chloride (DADMAC). In a preferred embodiment the cationic monomers are selected from [2-(acryloyloxy)ethyl]
30 trimethylammonium chloride (ADAM-Cl), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), and diallyldimethylammonium chloride (DADMAC). Quaternary amines are preferred cationic monomers because their charge is not pH dependent. More preferably the cationic monomer is [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl).

35 In one embodiment of a structurally modified, water-soluble glyoxylated polyacrylamide, the polyacrylamide is a copolymer originating from at most

30 mol-%, preferably at most 25 mol-%, and more preferably at most 20 mol-% of cationic monomers. Cationic polyacrylamide originating from at most 30 mol-% of cationic monomers have the benefit of easier metering compared to use of highly charged, cationic polymers, the use of which involves the challenge of exact metering and risk of over cationization of the paper machine circuit. Additionally, when synthesizing the polyacrylamide, lowering the amount of cationic monomers and increasing available acrylamide units may enhance the cross-linking rate such as glyoxylation rate of the polyacrylamide and the equilibrium of cross-linking. The cationicity of the polyacrylamide may have an effect on the strength response of paper. For example, cationic charges may decrease strength response of paper with fibre suspensions having low zeta-potential. Thus, in one embodiment the polyacrylamide is a copolymer originating from at most 10 mol-% of cationic monomers, based on the total monomer content. Typically, the polyacrylamide is a copolymer originating from 8-25 mol-% of cationic monomers.

The polyacrylamide used for preparing a structurally modified, water-soluble glyoxylated polyacrylamide may be an acrylamide containing polymer including acrylamide homopolymers, copolymers, and terpolymers including polyacrylamide; polyacrylamide derivatives; partially hydrolyzed polyacrylamide; partially hydrolysed polyacrylamide derivatives; methacrylamide homopolymers, copolymers, and terpolymers; diacetone acrylamide polymers; N-methylolacrylamide polymers; friction-reducing acrylamide polymers; and any combinations thereof. In one embodiment the polyacrylamide is PVAm obtained by partial or complete hydrolysis of poly(N-vinylformamide).

In one embodiment the method for manufacturing the aqueous composition of a structurally modified, water-soluble glyoxylated polyacrylamide further comprises buffering the aqueous medium before introducing glyoxal thereto. The pH of the aqueous composition is subsequently adjusted by buffering the composition by adding buffer solution thereto. In one embodiment the pH of the aqueous medium is adjusted to a value of at least 7.0, preferably to a value between 7.0 and 7.5, providing optimal pH for the cross-linking reaction of glyoxal. Additionally, the higher the pH, the higher is the degradation rate, especially when using reducing agents such as ferrous sulphate. In an

exemplary embodiment, the buffer is selected from carbonate buffers, phosphate buffers, acetate buffers, citrate buffers, formate buffers, tris buffers (tris=tris(hydroxymethyl)aminomethane), ftalate buffers, or any mixtures thereof.

5

Since the polyacrylamide backbone is degraded before and/or during the cross-linking, e.g. glyoxylation, a desired cross-linking level may be achieved without gelling the reaction mixture. In one embodiment the aqueous composition of a structurally modified water-soluble glyoxylated polyacrylamide has a bulk viscosity of at most 50 cP, preferably at most 20 cP, more preferably at most 15 cP, measured at 25 °C using Brookfield DVII T viscometer. When the bulk viscosity is at most 50 cP, the composition is easier to dose and over-flocculation is easier to avoid.

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15 The solids content of the aqueous composition of the structurally modified water-soluble glyoxylated polyacrylamide may be at most 5 weight-%, preferably at most 3 weight-%, and more preferably around 2 weight-%. By using such low solids contents high viscosities may be avoided thereby making the composition easier to handle and mix with the fibre suspension.

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In the present context, the term “fibre suspension”, into which drainage system is incorporated, is understood as an aqueous suspension which comprises fibres and optionally fillers. The fibre suspension may also be called pulp slurry or pulp suspension.

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In one embodiment the fibre suspension may comprise recycled fibre material and/or paper machine broke. In one embodiment, the recycled fibre material is selected from old corrugated cardboard, mixed office waste, double liner kraft, or any mixtures thereof. By old corrugated cardboard (OCC) is meant a material comprising corrugated containers having liners of test liner, jute or kraft, and it may cover also double sorted corrugated cardboard (DS OCC). By mixed office waste (MOW) is meant a material mainly containing xerographic papers and offset papers. By double lined kraft is meant a material comprising clean sorted unprinted corrugated cardboard cartons, boxes, sheet or trimmings, e.g. of kraft or jute liner. Presence of any of these in the fibre suspension decrease drainage and paper strength, and provide a substantial load of dissolved and colloidal substances to the

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process, interfering with the performance, especially of cationic retention and dry-strength agents, and wet-strength resins, as well as causing deposits. Conventionally increased washing has been used to reduce colloidal substances, however this operation is not desired nor typically available in
5 closed systems.

In one embodiment of the invention, a fibre suspension comprises at least 20 weight-%, preferably at least 30 weight-%, more preferably at least 40 weight-%, calculated as dry of recycled fibre material. The drainage system
10 of the present disclosure performs when using high amounts of recycled fibre materials, even up to 100 weight-%.

According to an embodiment of the invention, the fibre suspension has a conductivity of at least 2.0 mS/cm, preferably at least 2.5 mS/cm, and more
15 preferably at least 3.0 mS/cm, as measured at the headbox of the papermaking process. The conductivity of the fibre suspension may be even higher, such as at least 5.0 mS/cm. The drainage system according to the invention may perform even when added into a fibre suspension having conductivity of 10 mS/cm. It has been observed that the drainage system
20 according to the invention has good drainage performance in these conductivities, compared to a performance of traditional paper chemicals which start to lose their performance already at slightly elevated conductivities. The present invention continues performing well even in high conductivities.

25 According to an embodiment the fibre suspension comprises ash at least 10 weight-%, preferably at least 15 weight-%, more preferably at least 20 weight-% based on dry total solids. The ash may originate from added filler, and/or from fillers and/or mineral pigments of recycled fibre material, and/or
30 from paper machine broke. The amount of ash is calculated by drying the stock, and measuring the ash content. Standard ISO 1762, at temperature 525 °C is used for ash content measurements. Ash may be any filler or pigment conventionally used in paper and board making, such as ground calcium carbonate, precipitated calcium carbonate, clay, talc, gypsum,
35 titanium dioxide, synthetic silicate, aluminium trihydrate, barium sulphate, magnesium oxide or their any of mixtures. The drainage system of the

invention provides improved drainage and retention for high ash content fibre suspensions compared to the existing systems.

5 According to an embodiment of the invention, a drainage system is used for improving drainage of a fibre suspension comprising recycled fibre materials and having a conductivity of at least 2.0 mS/cm. According to an embodiment of the invention, a drainage system is used for improving drainage of a fibre suspension comprising recycled fibre materials including mixed office waste (MOW). Fibre suspensions comprising MOW have typically very high stock
10 conductivity level of at least 2.0 mS/cm, or higher. Recycled fibre materials comprising MOW have lower quality than e.g. chemical pulp also in other terms than conductivity, such as elevated content of ash and stickies, and lower fibre strength, increasing disturbances in the papermaking process.

15 The drainage system according to an embodiment of the present invention for manufacture of paper product or the like comprises inorganic siliceous microparticles, such as silica or bentonite or mixture thereof. According to an embodiment of invention, inorganic siliceous microparticles are selected from silica based particles, silica microgels, colloidal silica, silica sols, silica gels,
20 polysilicates, aluminosilicates, polyaluminosilicates, borosilicates, polyborosilicates, zeolites and swellable clays, such as bentonite. Preferably, inorganic siliceous microparticles are silica sols. These embodiments may provide improved retention and drainage, compared to other inorganic siliceous microparticles.

25 Silica sols may be characterized by their specific surface area (SSA) and/or level of aggregation or structuring. High SSA and structured or aggregated silica sols are beneficial in applications where flocculation is desirable. The degree of aggregation is normally characterized by the S-value, which is a
30 measure of the silica (as percent) in the disperse phase.

In one embodiment, the silica sol has either an S-value less than 40 %, preferably less than 35 %, or a specific surface area of at least 800 m²/g, preferably at least 900 m²/g. These embodiments may provide further
35 improved retention and drainage compared to silica sols with higher S-values or lower specific surface areas. According to an embodiment of the invention, the silica sol has both an S-value less than 40 % and a specific surface area

of at least 800 m²/g, preferably the S-value is less than 35 % and the specific surface area is at least 800 m²/g or at least 900 m²/g. These embodiments may provide even further improved retention, and drainage compared to silica sols with either the S-value or the specific surface area outside said
5 ranges.

The structurally modified, water-soluble glyoxylated polyacrylamide and inorganic siliceous microparticles may be introduced to the fibre suspension throughout the paper making process prior to the headbox of the paper
10 machine. In the process according to an embodiment of the invention, the inorganic siliceous microparticles and the structurally modified, water-soluble glyoxylated polyacrylamide may be added simultaneously into a fibre suspension. In the process according to a preferred embodiment of the invention, the inorganic siliceous microparticles and the structurally modified,
15 water-soluble glyoxylated polyacrylamide are added sequentially into a fibre suspension. In one embodiment, the structurally modified, water-soluble glyoxylated polyacrylamide polymer is added to a fibre suspension before the addition of the inorganic siliceous microparticles. In this embodiment the structurally modified, water-soluble glyoxylated polyacrylamide has more time
20 to adsorb onto the fibres before delivering to the headbox and the commencement of sheet forming, thereby providing higher strength improvement to the paper.

Typically, a fibre suspension having a consistency of above 20 g/l is called
25 thick stock, before it is diluted with white water into thin stock. In one embodiment, the structurally modified, water-soluble glyoxylated polyacrylamide is added into the fibre suspension at a consistency of above 20 g/l. Examples of possible addition points in a process for manufacturing paper or the like include any point after a machine chest, such as the suction
30 side of the machine chest pump, up to the point of thick stock dilution to obtain thin stock. In this embodiment the structurally modified, water-soluble glyoxylated polyacrylamide has not only more time to adsorb onto the fibres, but also is in closer proximity with the fibres due to the higher consistency, thereby providing opportunity for greater interaction, which provides a
35 strength improvement to the paper.

In one embodiment according to the invention, the inorganic siliceous microparticles are added into the fibre suspension after the last point of high shear before a headbox, preferably between a pressure screen and a headbox of the process. This embodiment has the benefit of improved
5 bridging of sheared polymer-fibre flocs by the inorganic siliceous microparticles, thereby improving retention and drainage.

Addition sequences may also include application of the structurally modified, water-soluble glyoxylated polyacrylamide after the inorganic siliceous
10 microparticles.

In one embodiment according to the invention, the drainage system further comprises a cationic flocculant. This embodiment has the benefit of further improved retention and drainage. The cationic flocculant may be a copolymer
15 of acrylamide and cationic monomers, or cationic starch. Preferably the cationic flocculant is a high molecular weight copolymer of acrylamide and cationic monomers (HMW CPAM) The cationic flocculant may be linear or branched. The cationic flocculant may be added directly to the fibre suspension or it may be added first to an aqueous flow, which is later
20 combined with the fibre suspension at any suitable location, for example at any suitable wet end location. Examples of such time points or locations include before or after refining of the fibre suspension, at the fan pump, before or at the head box. According to an embodiment, the cationic flocculant may be added into the fibre suspension in an amount of 0.1 - 2 lb
25 (dry solids)/ton dry fibre suspension.

In a specific embodiment of the paper or paperboard manufacturing process a structurally modified, water-soluble glyoxylated polyacrylamide is added into the fibre suspension, then a cationic flocculant is added, followed by
30 inorganic siliceous microparticles.

According to an embodiment of the invention, inorganic siliceous microparticles comprising silica sol is added into the fibre suspension in an amount of 0.1 to 2.0 lb (dry solids)/ton dry fibre suspension, such as 0.15 to
35 1.5 lb (dry solids)/ton dry fibre suspension, or 0.2 to 1.0 lb (dry solids)/ton dry fibre suspension. In one embodiment inorganic siliceous microparticles comprising bentonite is added to the fibre suspension in an amount of 0.2 to

10 lb (dry solids)/ton dry fibre suspension, such as 2 – 8 lb (dry solids)/ton dry fibre suspension, or 3 – 5 lb (dry solids)/ton dry fibre suspension. The slurry of inorganic siliceous microparticles, such as bentonite slurry or silica sol, may be further diluted before addition to the fibre suspension, if needed.

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In one embodiment according to the present invention, the structurally modified, water-soluble glyoxylated polyacrylamide is added to the fibre suspension in an amount of 1 – 20 lb (dry solids)/ton dry fiber suspension.

- 10 The invention relates to a process for the production of paper product or the like from a fibre suspension treated with the process according to the invention, wherein the treated fibre suspension is formed into a fibrous web and drained. The steps of forming a fibre suspension, draining and drying may be carried out in any suitable manner generally known to those skilled in
- 15 the art.

EXPERIMENTAL PART

Example 1

20

The aim of this example was to characterize glyoxylated polyacrylamide (GPAM) samples according to the invention in terms of molecular weight distribution (MWD) and moments (M_n , M_w , M_z) and intrinsic viscosity (IV) by using Gel Permeation Chromatography (GPC).

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Experimental Conditions:

- GPC system: Viscotek TDA 305, GPCmax VE 2001
- Detectors: UV, refractive index (RI), dual angle light scattering (90° and 7°), and differential viscometer
- 30 • Columns: Viscotek A7Guard 50 x 8.0 mm, PSS Novema Max ultrahigh, PSS Novema Max 100A
- Eluent: 0.6 M CH_3COOH + 0.1 M NaNO_3
- Flow rate: 0.7 mL/min
- Temperature: 30 °C
- 35 • Injection Volume: 100 μL

Theoretical background, some polymer characteristics computed in GPC context:

1. Concentration, C, from refractive index detector (RI) data, according to:

$$C = \frac{RI * CF}{dn/dc} \quad (1),$$

5

where CF is a constant of the detector, RI is the signal measured and dn/dc is the refractive index increment of the polymer in the NaNO_3 solvent used.

2. Molecular weight distribution (MWD) and moments of the distribution, M_n , M_w , M_z . Molecular weight, M, of a polymer in solution is computed from light scattering (LS) and RI data using the Rayleigh equation describes the relation of the scattered light of the dissolved polymer molecules by the so-called Raleigh ratio R_θ , of the polymer concentration and the molecular weight:

15

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)} + 2A_2c \quad (2),$$

where K is an optical constant, A_2 the second virial coefficient and $P(\theta)$ the structure factor. Next, the moments of distribution M_n , M_w , M_z are computed, using their defining equations.

20

3. Intrinsic viscosity, $[\eta]$, computed based on viscosity and RI data; the viscometer provides a signal proportional with the specific viscosity of the sample, η_{sp} , which together with the concentration from RI, allow $[\eta]$ calculation:

25

$$[\eta] = \frac{\eta_{sp}}{c} \quad (3).$$

Samples and the results of the GPC experiments made in 0.1 M NaNO_3 are presented in Table 1. A dn/dc value of 0.18 was used in computing MWD for all the samples.

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Table 1. Results from GPC experiments made in 0.1 M NaNO₃: moments of molecular weight distribution (MWD): M_n, M_w, M_z and intrinsic viscosity (IV).

Sample No.	M _n (g/mole)	M _w (g/mole)	M _z (g/mole)	M _w /M _n	IV (dl/g)
Novel GPAM1, 2 w-% solids (dry 20 mol-% cationic HMW PAM as backbone)	3.942x10 ⁵	1.319x10 ⁶	2.589x10 ⁶	3.346	1.569
Novel GPAM2, 2 w% solids (dry 10 mol-% cationic HMW PAM as backbone)	5.552x10 ⁵	1.177x10 ⁶	2.357x10 ⁵	2.120	1.817
Conventional low molecular weight GPAM, 7.5 w% solids (FB3000)	1.187x10 ⁶	4.372x10 ⁶	1.299x10 ⁷	3.685	0.350

As can be seen from Table 1, the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention (novel GPAM) exhibits far higher intrinsic viscosity, indicating a completely different molecular structure compared to a conventional GPAM (FB3000, Kemira Oyj). Additionally the polydispersity index is lower suggesting lower heterogeneity of sizes of the molecules.

Example 2

A 100% recycled fibre stock was diluted with white water to obtain a fibre suspension of 0.6 weight-% solids content. The mixed office waste (MOW) 100% recycled fibre stock had a very low freeness of 248 ml measured by Canadian Freeness Tester. The conductivity of the fibre suspension was high, 2800 µs/cm. As 400 mL diluted furnish was chemically treated in a Dynamic Drainage Analyzer (DDA) for vacuum drainage test. The vacuum of DDA was set in the range of -200 mbar to -300 mbar. The time needed to show a vacuum break was considered as the indication of drainage. In addition, the permeability expressed in pressure units (mbars) was also recorded and it is the indication of sheet porosity. The filtrate was used for

the measurement of turbidity by a Hach turbidimeter as an indication of retention.

In the study shown in Figure 1, each tested program contained 0.5 lb (dry solids)/ton silica sol ($SSA > 900 \text{ m}^2/\text{g}$, $S\text{-value} < 35 \%$) and 0.9 lb (dry solids)/ton high molecular weight cationic flocculant comprising a copolymer of acrylamide and cationic monomers (HMW CPAM). The tested programs further contained either no performance booster; or conventional GPAM FB3000; low molecular weight cationic flocculant comprising a copolymer of acrylamide and cationic monomers (LMW PAM); or the structurally modified, water-soluble glyoxylated polyacrylamide polymer according to the invention (Novel GPAM), as the booster. Among these programs, the structurally modified glyoxylated polyacrylamide exhibited much more interaction with the silica sol than the other cationic polymers in terms of the drainage time. The invention achieved an exceptional drainage improvement as shown in Figure 1.

Example 3

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A similar study was performed as in Example 2, using similar fibre suspension, conditions and procedures. To the fibre suspension was added either no processing aid program; or high molecular weight cationic flocculant comprising a copolymer of acrylamide and cationic monomers (HMW CPAM); HMW CPAM and silica; HMW CPAM, silica and conventional GPAM (FB3000); or HMW CPAM, silica and the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention (Novel GPAM), as the test program. The dosages were 0.5 lb (dry solids)/ton dry paper of silica sol ($SSA > 900 \text{ m}^2/\text{g}$, $S\text{-value} < 35 \%$), 0.9 lb (dry solids)/ton dry paper of HMW CPAM, and 3 lb (dry solids)/ton dry paper of FB3000 or the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention (Novel GPAM). The results are shown in Figure 2. From the results can be seen that the typical retention and drainage program, HMW CPAM and silica sol, provided improvement when compared to the HMW CPAM alone, and the performance of that program could be further boosted by addition of conventional GPAM. Again, the program using HMW CPAM and silica sol boosted with the structurally modified, water-soluble glyoxylated

polyacrylamide according to the invention (Novel GPAM), provided an exceptional drainage improvement when compared to any of the tested programs. A drainage improvement of this magnitude is highly exceptional, especially taking into account the low quality recycled fibre stock used in the preparation of the fibre suspension, and the high conductivity thereof, about 3 mS/cm.

Example 4

Yet another similar study was performed as in Example 2, using similar fibre suspension, conditions and procedures, but this time the fibre suspension was sized with ASA emulsion 5.5 lb (as is)/ton dry paper. ASA emulsion was prepared by a ratio of 1:1 for ASA:liquid starch as is. To the fibre suspension was added either no processing aid program; or conventional GPAM (FB3000); the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention (Novel GPAM); conventional GPAM and silica sol (FB3000 with silica); or the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention and silica sol (Novel GPAM with silica), as the test program. The dosages were 0.5 lb (dry solids)/ton dry paper of silica sol (SSA > 900 m²/g, S-value < 35 %), and 6 lb (dry solids)/ton dry paper of FB3000 or the structurally modified, water-soluble polyacrylamide polymer according to the invention. As shown in Figure 3, the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention alone (Novel GPAM) achieved comparable drainage results to a program of conventional GPAM and silica sol. When the structurally modified, water-soluble glyoxylated polyacrylamide according to the invention was used in combination with the silica sol, this program yielded the lowest drainage time, i.e. best result of drainage. Additionally it can be seen that this program performs well even without the use of HMW CPAM.

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Claims

1. A process for manufacturing paper product or the like comprising
 - providing a fibre suspension,
 - 5 - incorporating a drainage system into the fibre suspension, which drainage system comprises inorganic siliceous microparticles and a structurally modified, water-soluble glyoxylated polyacrylamide having an intrinsic viscosity at least 0.5 dl/g, preferably at least 0.7 dl/g and more preferably at least 1.0 dl/g, as determined by gel permeation
 - 10 chromatography (GPC), and
 - forming the fibre suspension into a fibrous web.
2. The process according to claim 1, wherein the fibre suspension comprises at least 20 weight-%, preferably at least 30 weight-%, more preferably at least 40 weight-%, calculated as dry, of recycled fibre material.
3. The process according to claim 1 or 2, wherein the fibre suspension has a conductivity of at least 2.0 mS/cm, preferably at least 2.5 mS/cm, and more preferably at least 3.0 mS/cm.
4. The process according to any of the preceding claims, wherein the inorganic siliceous microparticles comprise silica sol, bentonite or a mixture
- 15 thereof, preferably silica sol.
5. The process according to claim 4, wherein the silica sol has an S-value less than 40 %, preferably less than 35 %.
- 20 6. The process according to claim 4 or 5, wherein the silica sol has a specific surface area of at least 800 m²/g, preferably at least 900 m²/g.
7. The process according to any of the preceding claims, wherein a polydispersity index (M_w/M_n) of the structurally modified, water-soluble glyoxylated polyacrylamide is < 5.0, preferably < 4.0 and more preferably < 3.5, as determined by gel permeation chromatography (GPC).
- 25

8. The process according to any of the preceding claims, wherein the structurally modified, water-soluble glyoxylated polyacrylamide is a structurally modified, water-soluble glyoxylated cationic polyacrylamide.
9. The process according to any of the preceding claims, wherein the structurally modified, water-soluble glyoxylated polyacrylamide is an aqueous composition obtainable by
- (i) providing a polyacrylamide having a standard viscosity of at least about 1 cP, measured at 0.1 weight-% polymer concentration in 0.1 M NaCl, at 25 °C and pH 8.0 – 8.5, using Brookfield DVII T viscometer, in an aqueous medium,
 - 5 (ii) incorporating in said aqueous medium a degradation agent capable of reducing the standard viscosity of the polyacrylamide in the aqueous environment by cleaving a backbone of the polyacrylamide, and
 - (iii) cross-linking the polyacrylamide subjected to cleaving by introducing glyoxal to said aqueous medium for obtaining the aqueous composition of
 - 10 structurally modified, water-soluble glyoxylated polyacrylamide.
10. The process according to any of the preceding claims, wherein the inorganic siliceous microparticles and the structurally modified, water-soluble glyoxylated polyacrylamide are added sequentially into the fibre suspension.
11. The process according to claim 10, wherein the structurally modified, water-soluble glyoxylated polyacrylamide is added prior to the addition of the inorganic siliceous microparticles.
12. The process according to any of the preceding claims, wherein the inorganic siliceous microparticles are added into the fibre suspension after a last point of high shear before a headbox, preferably between a pressure screen and a headbox of the process.
13. The process according to any of the preceding claims, wherein the drainage system further comprises a cationic flocculant, preferably a copolymer of acrylamide and cationic monomers, or cationic starch.

14. A drainage system for improving drainage in manufacturing of paper product or the like, wherein the drainage system comprises inorganic siliceous microparticles and a structurally modified, water-soluble glyoxylated polyacrylamide having an intrinsic viscosity at least 0.5 dl/g, preferably at least 0.7 dl/g and more preferably at least 1.0 dl/g, as determined by gel permeation chromatography (GPC).

15. The drainage system according to claim 14, wherein a polydispersity index (M_w/M_n) of the structurally modified, water-soluble glyoxylated polyacrylamide is < 5.0 , preferably < 4.0 and more preferably < 3.5 , as determined by gel permeation chromatography (GPC).

16. The drainage system according to claim 14 or 15, wherein the structurally modified, water-soluble glyoxylated polyacrylamide is a structurally modified, water-soluble glyoxylated cationic polyacrylamide.

17. The drainage system according to any of the preceding claims 14 to 16, wherein the structurally modified, water-soluble glyoxylated polyacrylamide is an aqueous composition obtainable by

- (i) providing a polyacrylamide having a standard viscosity of at least about 1 cP, measured at 0.1 weight-% polymer concentration in 0.1 M NaCl, at 25 °C and pH 8.0 – 8.5, using Brookfield DVII T viscometer, in an aqueous medium,
- (ii) incorporating in said aqueous medium a degradation agent capable of reducing the standard viscosity of the polyacrylamide in the aqueous environment by cleaving a backbone of the polyacrylamide, and
- (iii) cross-linking the polyacrylamide subjected to cleaving by introducing glyoxal to said aqueous medium for obtaining the aqueous composition of structurally modified, water-soluble glyoxylated polyacrylamide.

18. The drainage system according to any of the preceding claims 14 to 17, wherein the inorganic siliceous microparticles comprise silica sol, bentonite or a mixture thereof, preferably silica sol.

19. The drainage system according to claim 18, wherein the silica sol has an S-value less than 40 %, preferably less than 35 %.

20. The drainage system according to claim 18 or 19, wherein the silica sol has a specific surface area of at least 800 m²/g, preferably at least 900 m²/g.

- 5 21. A paper product comprising the drainage system according to any of the preceding claims 14 to 20, or manufactured by the process according to any of the preceding claims 1 to 13.

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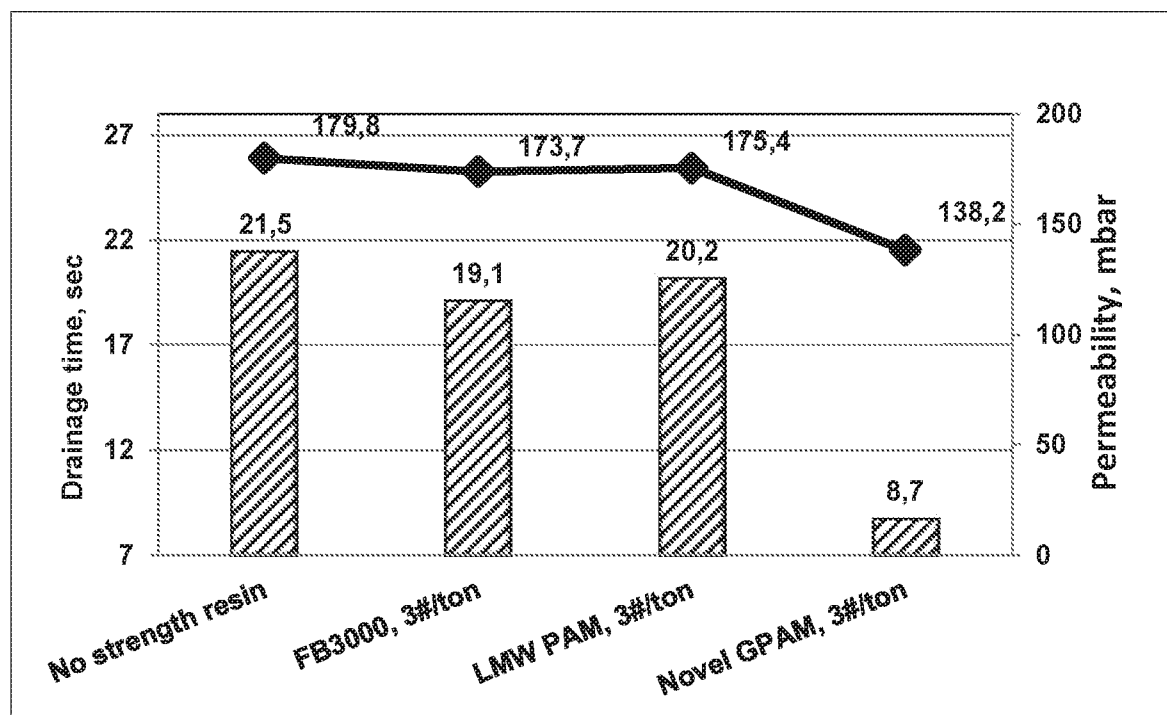


Fig. 1

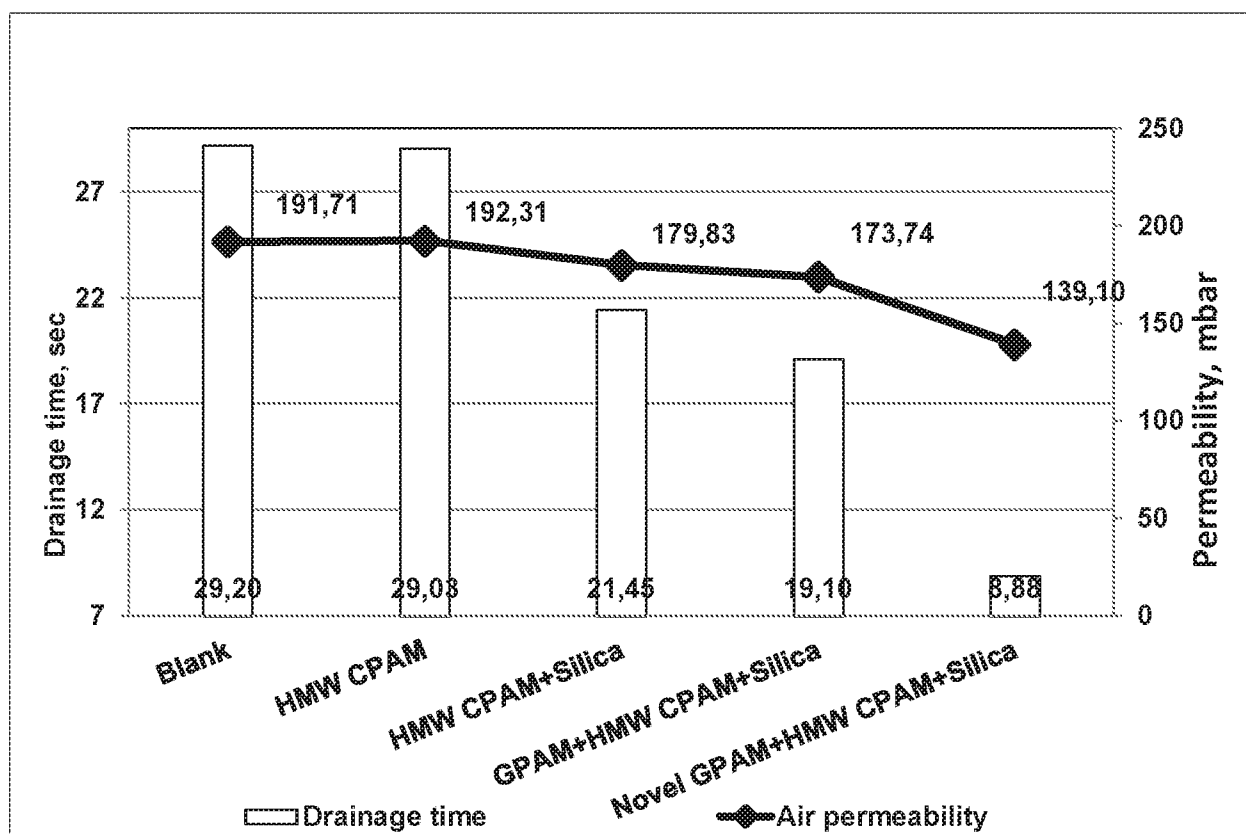


Fig. 2

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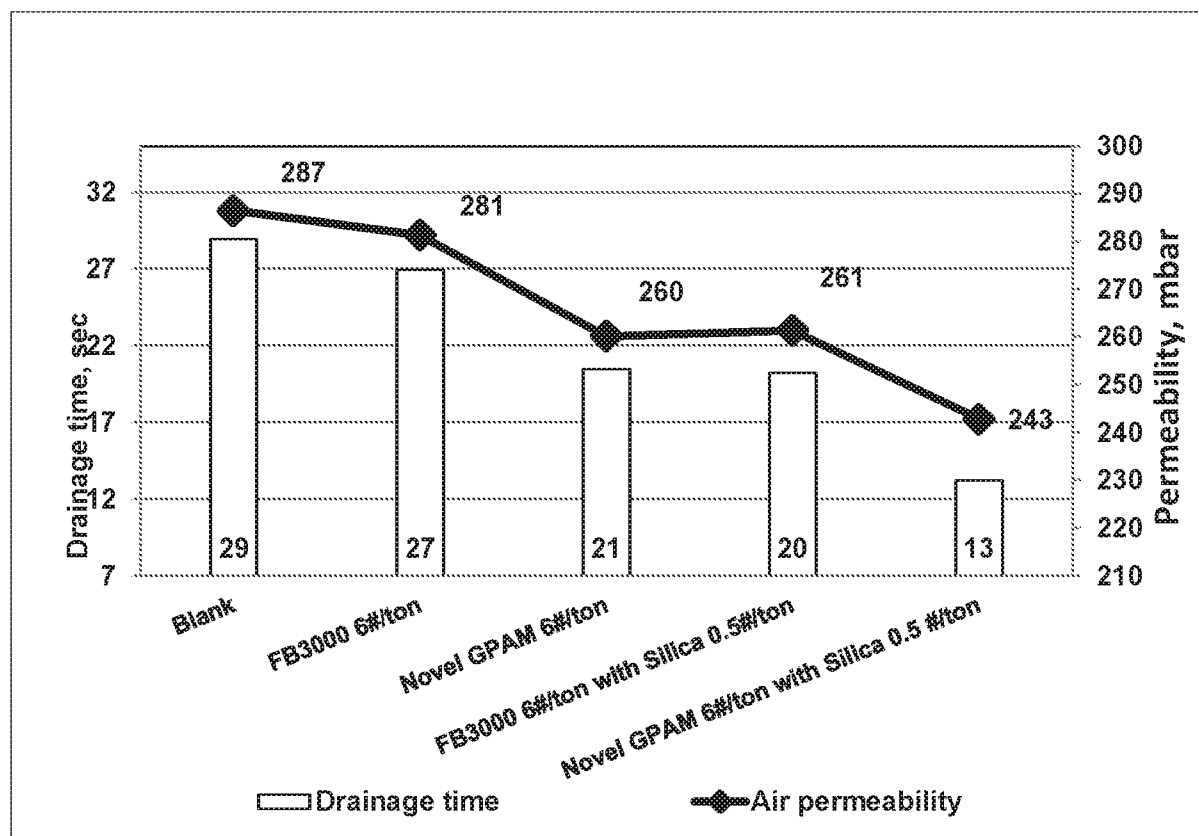


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/054630

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H17/37 D21H17/68 D21H21/10
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21H

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

6 June 2017

Date of mailing of the international search report

22/06/2017

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/054630

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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