

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization

International Bureau

(43) International Publication Date  
31 May 2018 (31.05.2018)



(10) International Publication Number  
**WO 2018/097822 A1**

(51) International Patent Classification:

*D21H 17/37* (2006.01)      *D21H 21/20* (2006.01)  
*D21H 21/18* (2006.01)      *D21H 17/38* (2006.01)

Published:

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

(21) International Application Number:

PCT/US2016/063445

(22) International Filing Date:

23 November 2016 (23.11.2016)

(25) Filing Language:

English

(26) Publication Language:

English

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

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

(54) Title: A PAPER STRENGTH SYSTEM AND A PROCESS OF MAKING PAPER OR THE LIKE

(57) Abstract: A paper strength system for improving paper strength in manufacturing of paper or the like, wherein the paper strength system comprising a structurally modified, water-soluble aldehyde functionalized 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, determined by gel permeation chromatography (GPC), and a second polymer comprising amine groups or hydroxyl groups. The invention relates also a process for manufacturing paper or the like, wherein the paper strength system is incorporated into the fibre suspension.



WO 2018/097822 A1

## A PAPER STRENGTH SYSTEM AND A PROCESS OF MAKING PAPER OR THE LIKE

### **Field of the invention**

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The present invention relates to a paper strength system and a process of making paper or the like according to the preambles of the independent claims presented below.

### **Background of the invention**

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Paper sheets are made by dewatering a pulp suspension, forming a uniform web, and drying the web. Due to the increased environmental awareness and regulations, papermaking processes have become more and more closed using  
15 less fresh water, resulting in increased accumulation of detrimental substances such as anionic trash, and salts increasing total ionic strength and conductivity in the fibre suspension and process waters. Concurrently, the recycled fibre content has increased as a fibre source in the papermaking. Paper or board, which is made from fibre stock comprising extensive amounts of recycled fibres,  
20 has typically low dry strength properties, because the quality of fibres is reduced during the recycling. Normally the low strength properties are improved with various strength additives. Additionally, 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  
25 agents, dissolved and colloidal substances, including anionic substances, so called anionic trash. These substances carried over to the papermaking process may further increase the overall colloidal load and conductivity of the fibre suspension, accumulating in the process water circuit. The efficiency of the conventional strength additives usually is deteriorated in the presence of the  
30 detrimental substances or high conductivities. Especially anionic trash consumes strength additives as these may interact with the anionic trash instead of the fibres. At the same time the recycled fibres show relatively low charge levels, which means that the interaction between the fibres and the strength

additives is not as effective as with virgin fibres. Consequently, there is an increasing demand to maintain the efficiency of strength additives.

Glyoxylated polyacrylamides (GPAMs) are typically used as strength increasing additives in the paper making industry. Strength performance of conventional  
5 GPAM may be adversely affected by relatively high pH and high levels of alkalinity, when present as bicarbonate ions. The performance loss of conventional GPAM caused by slightly elevated alkalinity of the fibre suspension may be compensated by using amine containing polymers such as polyamidoamine epichlorohydrin (PAE) as booster. However, the dry strength  
10 performance loss of conventional GPAM and PAE in further elevated alkalinity may be even steeper than the performance loss of conventional GPAM alone.

Thus, there is a constant need for chemical additive systems providing improved paper strength, and preferably tolerating the challenging conditions such as  
15 elevated conductivity and/or presence of elevated amounts of detrimental substances without substantial performance loss.

### **Summary of the Invention**

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

One object of the present invention is to provide a process for manufacturing paper or the like with improved paper strength performance. More detailed, the  
25 object of the present invention is to provide a use of a structurally modified, water-soluble aldehyde functionalized polyacrylamide in a papermaking process for improving paper strength.

The object of the present invention is especially to provide a process for  
30 manufacturing paper or the like with improved strength performance, when using fibre suspension having elevated alkalinity.

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

In order to achieve among others the objects presented above, the invention is characterized by what is presented in the characterizing parts of the enclosed independent claims.

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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.

10 The embodiments and advantages mentioned in this text relate, where applicable, both to the paper strength system, the process as well as to the uses according to the invention, even though it is not always specifically mentioned.

15 Typical paper strength system according to the invention for improving paper strength in manufacturing of paper or the like, wherein the paper strength system comprises

- 20 - a structurally modified, water-soluble aldehyde functionalized 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, determined by gel permeation chromatography (GPC), and
- a second polymer comprising amine groups or hydroxyl groups.

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

- 25 - providing a fibre suspension,
  - incorporating a paper strength system into the fibre suspension, which paper strength system comprises
    - 30 (i) a structurally modified, water-soluble aldehyde functionalized 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, determined by gel permeation chromatography (GPC), and
    - (ii) a second polymer comprising amine groups or hydroxyl groups,
- and
- forming the fibre suspension into a fibrous web.

Typical paper product comprises the paper strength system according to invention, or it is manufactured by the process according to the invention. As used herein, by expression paper or the like, or a paper product, is meant any sheet material comprising cellulosic fibres, such as printing and writing papers, industrial papers, tissue papers, paperboards, cardboards, packaging papers, wrapping papers, paper adhesive tapes, paper bags, paper cloths, towels, wallpapers, carpet backings, paper filters, decorative papers, etc.

Now it has been surprisingly found that the performance of a structurally modified, water-soluble aldehyde functionalized 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, determined by gel permeation chromatography (GPC), is significantly improved when used in combination with a second polymer comprising amine groups or hydroxyl groups.

According to one preferred embodiment of the invention, the structurally modified, water soluble aldehyde functionalized polyacrylamide is glyoxylated polyacrylamide (GPAM), preferably a glyoxylated cationic polyacrylamide. A glyoxylation of the polyacrylamide creates aldehyde functionality to the polyacrylamide. Aldehydes may react with the amine groups or the hydroxyl groups present in the second polymer. The amine groups may be primary, secondary and/or tertiary amine groups, preferably the amine groups are primary and/or secondary amine groups, as these are capable of reacting with the aldehyde groups in the structurally modified, water soluble aldehyde functionalized polyacrylamide quickly, without requiring any special reaction conditions. Aldehydes may react for example with primary amines of the second polymer thereby forming imines or Schiff bases, or aldehydes may react for example with secondary amines of the second polymer thereby forming enamines.

As the result of the reaction between aldehyde groups of the structurally modified water soluble aldehyde functionalized polyacrylamide, such as GPAM, and amine groups or hydroxyl groups of the second polymer, polymers with

even higher molecular weight and more developed structure are formed. The increased molecular weight and/or structure improve performance as strength agents in papermaking. In addition, as especially the reaction between aldehydes and primary and/or secondary amines is fast and does not require special conditions, the paper strength system according to the invention may be prepared right before the addition to the pulp slurry.

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

- 10 (i) providing a polyacrylamide having a standard viscosity of at least about 1 cP, measured at 0.1 weight-% polymer concentration in 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
- 15 (iii) cross-linking the polyacrylamide subjected to cleaving by introducing a polyaldehyde cross-linking agent, such as glyoxal, to said aqueous medium for obtaining an aqueous composition of the structurally modified, water-soluble aldehyde functionalized polyacrylamide, such as glyoxylated polyacrylamide.

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Thus, by the above described method higher molecular weight may be achieved compared to the conventional GPAM polymers, typically manufactured by glyoxylating low molecular weight cationic polyacrylamide based polymers obtained by solution polymerization.

25

As already discussed above, strength performance of conventional GPAM can be adversely affected by e.g. relatively high pH and high levels of alkalinity, when present as bicarbonate ions. The performance loss of conventional GPAM caused by slightly elevated alkalinity of the fibre suspension may be compensated by using amine containing polymers such as polyamidoamine epichlorohydrin (PAE) as booster. However, the dry strength performance loss of conventional GPAM and PAE in further elevated alkalinity may be even steeper than the performance loss of conventional GPAM alone. Now, it has

30

been found that the structurally modified, water soluble aldehyde-functionalized polyacrylamide, e.g. the structurally modified GPAM, provides unexpected strength performance in elevated alkalinity when used in combination with a second polymer comprising amine groups or hydroxyl groups. Preferably the second polymer is a cationic polymer. When the second polymer is cationic, at least part thereof may bind to anionic trash thereby reducing the adsorption of the structurally modified, water soluble aldehyde functionalized polyacrylamide to the anionic trash instead of fibres, thereby enhancing strength performance. When the second polymer is cationic, it may also contribute to the charge control of the papermaking process. More preferably the second polymer comprises primary and/or secondary amine groups. The primary and/or secondary amine groups provide cationicity to the second polymer, and as their reaction with the aldehyde groups of the structurally modified, water soluble aldehyde functionalized polyacrylamide is quick and easy, polymer complexes with an enhanced molecular weight and structure are readily obtained, thereby further enhancing the strength performance of the system. The strength performance of the structurally modified water-soluble aldehyde functionalized polyacrylamide and the second polymer is even further increased when the alkalinity of the fibre suspension is further elevated, especially in case of structurally modified GPAM and second polymer comprising primary and/or secondary amine groups.

It is believed that the exceptional performance of the structurally modified aldehyde functionalized polyacrylamide, such as GPAM, and the second polymer comprising amine groups or hydroxyl groups as strength agents in papermaking, especially in the challenging condition of elevated alkalinity and/or hardness, is due to the higher molecular weight of the structurally modified GPAM and/or its unique structure compared to conventional GPAMs, although exact mechanism is not known.

Especially, the better performance may be provided when polyamine, polyamidoamine (PAA), polyamidoamine epihalohydrin (PAE), polyethyleneimine (PEI), polyvinylamine or any combination thereof are used as the second polymer comprising primary and/or secondary amine groups.

Preferably, the polyamidoamine epichlorohydrin (PAE) is used in combination with the structurally modified water soluble aldehyde functionalized polyacrylamide, such as GPAM, 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, determined by gel permeation chromatography (GPC).

All paper grades and the like may benefit from the paper strength system according to the present invention, especially packaging paper or board, copy paper or the like. Especially beneficial the novel system is for paper grades for which easy repulping and recyclability is desired, and/or for papermaking processes where the fibre suspension has elevated alkalinity and/or hardness.

#### **Brief description of the figures**

Figures 1- 6 show the variability charts of different strength studies according to Example 2, achieved using alone a conventional GPAM and the polymer according to the invention (ultra-high molecular weight, UHMW, GPAM) as a strength resin, and using a conventional GPAM and UHMW GPAM in combination with a strength booster (partially crosslinking polyamidoamine epichlorohydrin, which has a molar ratio of epichlorohydrin to amine  $< 0.4$ ) at different alkalinities of the fibre suspension.

#### **Detailed description of the invention**

In the context of the present application the term "aldehyde-functionalized polyacrylamide" denotes a polyacrylamide carrying aldehyde groups in the polymer molecule. For example crosslinking a polyacrylamide with a polyaldehyde, such as dialdehyde, trialdehyde etc., such as glyoxylation of a polyacrylamide, creates aldehyde functionality to the polyacrylamide

The term "water-soluble" is understood in the context of the present application that the aldehyde functionalized polyacrylamide is fully miscible with water. When mixed with an excess of water, the aldehyde functionalized polyacrylamide in the paper strength system is preferably fully dissolved and the



obtained polymer solution is preferably essentially free from discrete polymer particles or granules. Excess of water means that the obtained polymer solution is not a saturated solution.

5 Standard viscosity is used herein to reflect or indicate the molecular weights for polymers having molecular weights more than 1 million Dalton. Standard 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  
10 11.7 weight-% NaCl in a 250 mL beaker, i.e. 0.1 weight-% polymer concentration in 1 M NaCl. Then, pH of the 0.1 weight-% salt dilute polymer solution is adjusted to pH 8.0 - 8.5 by dilute NaOH solution or H<sub>2</sub>SO<sub>4</sub> 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  
15 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, 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  
20 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 viscosity is equally centipoise (cP).

A backbone of a polyacrylamide refers in this disclosure to the main chain of the  
25 polyacrylamide which is a result of the (co)polymerisation reaction of acrylamide, and optionally any cationic, anionic or non-ionic monomers 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  
30 chain is substantially linear chain to which all other chains may be regarded as pendant.

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 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  
5 comprising the polyacrylamide.

As used herein, the term "cross-linking" refers to covalently linking two target groups present in the polyacrylamide and/or in the fragments thereof, which fragments are resulted from the cleaving of the polyacrylamide backbone.  
10 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.

Preferably, the structurally modified, water-soluble aldehyde functionalized polyacrylamide, such as glyoxylated polyacrylamide, is an aqueous composition  
15 obtained by

- (i) providing a polyacrylamide having a standard viscosity of at least about 1 cP, measured at 0.1 weight-% polymer concentration in 1 M NaCl, at 25 °C and pH 8.0 – 8.5, using Brookfield DVII T viscometer, in an aqueous medium,
- 20 (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 a polyaldehyde cross-linking agent, such as glyoxal, to said aqueous medium  
25 for obtaining an aqueous composition of the structurally modified, water-soluble aldehyde functionalized polyacrylamide, such as glyoxylated polyacrylamide.

When a structurally modified, water-soluble aldehyde functionalized polyacrylamide is prepared by the method disclosed above, the aldehyde  
30 functionalized polyacrylamide, such as glyoxylated polyacrylamide, may be obtained in the form of an aqueous, non-gelled composition surprisingly expressing a synergistic interaction with a second polymer having amine groups or hydroxyl providing unexpected strength performance, even in elevated

alkalinity of the fibre suspension, such as above 100 ppm, expressed as  $\text{CaCO}_3$ , commonly known to adversely affect aldehyde functionality on the aldehyde functionalized polyacrylamide.

5 In one embodiment of the invention, the polyacrylamide used in the method for preparing a structurally modified water-soluble aldehyde functionalized polyacrylamide 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 1 M NaCl, at 25 °C, pH 8.0-8.5, using Brookfield DVII T  
10 viscometer. Higher standard viscosity of the polyacrylamide corresponds to higher molecular weight. High molecular weight polymers are available in higher 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  
15 may have higher molecular weight. Typically, the polyacrylamide has a molecular weight of at least 2 million Dalton, preferably 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  
20 polyacrylamide is a dry polymer which allows for improved logistics both cost and product robustness for challenging climate conditions.

In the preparing of a structurally modified, water-soluble aldehyde functionalized polyacrylamide of the paper strength system, the degradation agent and the  
25 cross-linking agent may be pre-mixed together before addition, or they may be added separately such as sequentially, the degradation agent being added before the cross-linking agent, such as glyoxal. The additions of the degradation agent and the cross-linking agent may also overlap, in which case the addition of the degradation agent may continue when the cross-linking addition is started.  
30 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 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 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 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 aldehyde functionalized 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 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 degradation agent.

In one embodiment of preparing a structurally modified, water-soluble aldehyde functionalized polyacrylamide, step (iii) of the method is initiated after all degradation agent has been incorporated to the aqueous medium in step (ii) 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 aldehyde functionalized polyacrylamide.

The degradation agent used in the method for preparing a structurally modified, water-soluble aldehyde functionalized 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.

5 This has the effect of reducing the standard viscosity of the polyacrylamide, 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

10 polymeric fragments thereof.

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 %. 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

15 degradation agent.

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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 reducing degradation agent is selected from the group consisting of an iron compound, tin(II) chloride, sodium borohydride ( $\text{NaBH}_4$ ), 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 embodiment the degradation agent is selected from the group consisting of an iron compound, sodium borohydride ( $\text{NaBH}_4$ ), sodium dithionite, sodium percarbonate, sodium persulfate, potassium persulfate, ammonium persulfate, hydrogen peroxide, sodium perborate, to avoid incorporating chlorides.

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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  
5 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 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  
10 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 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  
15 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 combinations thereof.

The most advantageous polymer degradation agent for use in the present  
20 disclosure is iron(II)sulfate. Iron sulfate, in particular ferrous sulfate, is able to dissolve and degrade at ambient pulp suspension conditions whereas the 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  
25 advantageously selected from the group consisting of persulfates, peroxides, sodium chlorite, tin(II)chloride and percarbonates.

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  
30 dry. In case the degradation agent contains crystal water, the expression calculated as dry includes the crystal water. In this range the degradation of 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 polyaldehyde cross-linking agent is a dialdehyde cross-linking agent providing aldehyde functionality to the cross-linked polyacrylamide, rendering the polyacrylamide cellulose-reactive. The polyaldehyde cross-linking agent may also have more than two aldehydes, for example it may be a trialdehyde. The polyaldehyde cross-linking agent may have two or more carbon atoms, such as three or more carbon atoms, such as glyoxal, malondialdehyde, succindialdehyde, glutaraldehyde etc. 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 atoms.

15 The cross-linking reaction of preparing a structurally modified, water-soluble aldehyde functionalized polyacrylamide, such as glyoxylation in the present disclosure may be any known or obvious glyoxylation sequence. An example 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 20 from about 7 to 8, and by stabilizing under acidic conditions pH from about 3 to 6.

In one embodiment the amount of glyoxal is from 5 to 80 weight-%, preferably 25 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 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 30 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.

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. Polyaldehyde cross-linking agents such as glyoxal may react with the amide groups of the acrylamide. Thus, the 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.

In one preferred embodiment of a structurally modified, water-soluble aldehyde functionalized 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 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 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 aldehyde functionalized 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 (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] 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).

In one embodiment of a structurally modified, water-soluble aldehyde functionalized 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 aldehyde functionalized 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 aldehyde functionalized 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  
5 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, formiate buffers, tris buffers (tris=tris(hydroxymethyl)aminomethane), ftalate buffers, or any mixtures thereof.

10 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 aldehyde functionalized polyacrylamide has a  
15 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.

20 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.

25 Typically a structurally modified, water-soluble aldehyde functionalized 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,  
30 water-soluble aldehyde functionalized polyacrylamide has preferably been obtained by the method described in the present 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 aldehyde functionalized polyacrylamide, such as 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 aldehyde functionalized polyacrylamide according to the invention is at least  $0.5 \text{ Mg/mol}$ , preferably at least  $0.7 \text{ Mg/mol}$  and more preferably at least  $1.0 \text{ Mg/mol}$ . A number average molar mass ( $M_n$ ) of a structurally modified, water-soluble aldehyde functionalized polyacrylamide according to a typical embodiment of the invention is at least  $2.8 \times 10^5 \text{ g/mol}$ , preferably at least  $3.0 \times 10^5 \text{ g/mol}$  and more preferably at least  $3.2 \times 10^5 \text{ g/mol}$ .  $M_w$ ,  $M_n$  and polydispersity index ( $M_w/M_n$ ) are determined by GPC. The GPC system and measurement conditions are described more detailed in Example 1.

According to one preferred embodiment, the structurally modified, water soluble aldehyde functionalized polyacrylamide is made on site. Thus, the present invention provides logistical benefits and also strength benefits as there is no risk of deterioration of the structurally modified, water-soluble aldehyde functionalized polyacrylamide caused by storing.

The paper strength system according to the invention comprises a second polymer comprising amine groups or hydroxyl groups. Preferably, the second polymer is a cationic polymer. More preferably the second polymer comprises primary and/or secondary amine groups. According to a preferred embodiment of the invention, the second polymer has a molecular weight in the range of  $50\,000 - 5\,000\,000 \text{ g/mol}$ , preferably  $100\,000 - 2\,000\,000 \text{ g/mol}$ , which provides the desired high molecular weight and the structure of the polymer formed as a result of the reaction between aldehyde groups of the structurally modified water soluble aldehyde functionalized polyacrylamide, such as GPAM, and amine groups or hydroxyl groups of the second polymer.

According to an embodiment of the invention, the second polymer comprising primary and/or secondary amine groups is selected from the group consisting of polyamine, polyamidoamine (PAA), polyamidoamine epihalohydrin (PAE), polyethyleneimine (PEI), polyvinylamine and any combination thereof. According

to a preferred embodiment of the invention, the second polymer is polyamidoamine epihalohydrin (PAE).

In one preferred embodiment of the invention, the second polymer comprising  
5 primary and/or secondary amine groups is polyamidoamine epihalohydrin (PAE)  
having a molar ratio of epihalohydrin to amine in the range of 0.03 to 1.5,  
preferably 0.1 to 1.3 or more preferably 0.15 to 0.8. A molar ratio of  
epihalohydrin to amine of more than 0.8, such as more than 0.9 or more than  
1.0, i.e. a so-called crosslinking PAE, may provide both permanent wet strength  
10 and dry strength to the paper. A molar ratio of epihalohydrin to amine of at most  
0.8, such as at most 0.6, or at most 0.5, i.e. a so-called partially or non-  
crosslinking PAE, may provide primarily dry strength to the paper.

According to an embodiment of the invention solids content of an aqueous  
15 composition of the second polymer is at least 15 weight-%, preferably at least 20  
weight-%. When the second polymer comprising primary and/or secondary  
amine groups, especially polyamidoamine epihalohydrin (PAE), has the solids  
content at least 15 weight-%, preferably at least 20 weight-%, when combining  
with the structurally modified aldehyde functionalized polyacrylamide of the  
20 invention, the strength performance such as dry tensile and initial wet tensile is  
even better. It is believed that the higher solids content of the second polymer  
provides improved interaction and/or higher reaction rate with the structurally  
modified aldehyde functionalized polyacrylamide of the invention and thus more  
favorable molecular weight and/or structure to the reaction product.

25  
According to an embodiment of the invention, the paper strength system  
comprises the structurally modified, water-soluble aldehyde functionalized  
polyacrylamide and the second polymer in a weight ratio of 1:100 to 100:1,  
preferably 1:50 to 50:1, more preferably 1:10 to 10:1, as dry solids. The optimal  
30 weight ratio may vary depending on the amount of aldehyde groups in the  
aldehyde functionalized polyacrylamide and the amount of amine groups or  
hydroxyl groups in the second polymer. In some embodiments, it may be  
beneficial to have excess of the second polymer, so that part of the second  
polymer is not reacted with the aldehyde functionalized polyacrylamide, but it

may be consumed by anionic trash or provide charge control. In some embodiments, it may be beneficial to have excess of the aldehyde functionalized polyacrylamide, so that part of the aldehyde functionalized polyacrylamide is not reacted with the second polymer, thereby having more free aldehyde groups to

5 react with cellulose fibres. Better strength responses may be obtained when the amount of the aldehyde functionalized polyacrylamide is higher than the amount of the second polymer. According to an embodiment of the invention, the paper strength system comprises the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer in a weight ratio of more

10 than 1:1, as dry solids. According to an embodiment of the invention, the paper strength system comprises the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer in a weight ratio of more than 1:1 to 50:1, such as more than 1:1 to 20:1, preferably 2:1 to 9:1, more preferably in a weight ratio of 2:1 to 3:1, as dry solids.

15

In the present context, the term "fibre suspension", into which the paper strength 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. The fibre suspension may comprise any fibres. In

20 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. In some embodiments the fibre suspension may comprise even > 70 weight-%, sometimes even > 80 weight-%, of fibres originating from recycled fibre material. The paper strength system of

25 the present invention performs even when using high amounts of recycled fibre materials, even up to 100 weight-%.

The paper strength system according to the invention may significantly improve the dry and wet strength performance of the structurally modified water-soluble

30 aldehyde functionalized polyacrylamide at increasing alkalinity of the environment. The dry and wet strength performance may also be maintained at increased alkalinity of the environment by using the paper strength system according to the present invention. According to an embodiment of the invention, an alkalinity of the fibre suspension is at least 100 ppm, preferably at least 200

ppm, such as in the range of 100 - 1000 ppm, preferably 200-600 ppm, calculated as CaCO<sub>3</sub>.

5 An embodiment may include, but is not limited to use of the paper strength system of the present invention at the liquid environment with acidic to alkaline pH, e.g. pH 5-8, elevated hardness, elevated chlorine residual, and/or elevated sulfite residual. All of these are known to negatively affect the wet-end process and performance of conventional papermaking additive systems.

10 According to one embodiment of the invention the paper strength system is added to fibre suspension having a hardness of at least 100 ppm expressed as CaCO<sub>3</sub>, preferably hardness of at least 200 ppm expressed as CaCO<sub>3</sub>, more preferably hardness of at least 300 ppm expressed as CaCO<sub>3</sub>, such as 100 – 1000 ppm, preferably 200 – 600 ppm. The hardness means here total hardness,  
15 i.e. including Mg and Ca ions.

The paper strength system of the invention may also provide improvements to drainage and drying efficiency, as well as to retention. Additionally, it may be useful in pre-treating fillers or fibres before incorporating them into a  
20 papermaking process.

The paper strength system of the invention may also be useful as retention or fixing system in a papermaking process for controlling any hydrophobic substances such as stickies, wood and white pitch.  
25

The structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer are preferably pre-mixed prior to the addition into the fibre suspension, thereby further enhancing the molecular weight and the structure of the reaction product, and thus the strength performance of the  
30 system. According to an embodiment of the invention, the premixed solution of the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer is diluted to at most 0.5 weight-%, preferably at most 0.1 weight-%, as dry solids prior to the addition to fibre suspension.

Typically, the premixed solution of the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer may be added to the fibre suspension having a consistency of below 20 g/l, i.e. so-called thin stock.

5

The premixed solution of the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer may be added into the fibre suspension at any point prior to fan pump.

10

The invention relates to a process for the production of paper product or the like from a cellulosic 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 the art.

15

In one embodiment the components of the paper strength system of the present invention are used as an additive system in an aqueous flow in the field of oil and mining, for example as a dewatering aid subsequently providing dispersion stability. Aqueous flows to be treated with the additive system may include e.g.

20

an aqueous flow of a mineral processing or an aqueous well-treatment fluid.

A better understanding of the present invention may be obtained through the following examples which are set forth to illustrate, but are not to be construed as the limit of the present invention.

25

## EXPERIMENTAL PART

**Example 1**

5 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 (Mn, Mw, Mz) and intrinsic viscosity (IV) by using Gel Permeation Chromatography (GPC).

10 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
- Columns: Viscotek A7Guard 50 x 8.0 mm, PSS Novema Max ultrahigh, 15 PSS Novema Max 100A
- Eluent: 0.6 M CH<sub>3</sub>COOH + 0.1 M NaNO<sub>3</sub>
- Flow rate: 0.7 mL/min
- Temperature: 30 °C
- Injection Volume: 100 μL

20

Theoretical background, some polymer characteristics computed in GPC context:

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

25

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

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<sub>3</sub> solvent used.

30

2. Molecular weight distribution (MWD) and moments of the distribution, Mn, Mw, Mz. 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  $R_{\theta}$ , of the polymer concentration and the molecular weight:

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

5

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.

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

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

15

Samples and the results of the GPC experiments made in 0.1 M  $\text{NaNO}_3$  are presented in Table 1. A  $dn/dc$  value of 0.18 was used in computing MWD for all the samples.

20

Table 1. Results from GPC experiments made in 0.1 M NaNO<sub>3</sub>: moments of molecular weight distribution (MWD): M<sub>n</sub>, M<sub>w</sub>, M<sub>z</sub> and intrinsic viscosity (IV).

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

10

## Example 2

### Preparation of the chemical blend

The structurally modified, water-soluble glyoxylated polyacrylamide according to the invention (UHMW GPAM) and strength booster (partially crosslinking polyamidoamine epichlorohydrin, which has a molar ratio of epichlorohydrin to amine < 0.4) was blended with 2:1 ratio as dry solids. UHMW GPAM is used immediately after it was made-down and blended with the strength booster as received for a minimum of 2 minutes using magnetic stirrer. It is then diluted to 1% prior to the addition to fibre suspension. The structurally modified, water-soluble glyoxylated polyacrylamide (UHMW GPAM) was prepared by dissolving

20

and degrading cationic HMW PAM backbone (15 mol-% cationic monomers) in water with 500 ppm of iron(II)sulfate, and then glyoxylating with 25 weight-% of glyoxal (as dry).

5 Handsheet procedure

Handsheet studies were conducted using the thick stock which was a recycled brown furnish. The thick stock was diluted with the white water from the same machine and/or the synthetic water treated with 100 ppm of sulfate and 35 ppm of calcium ion. The hardness of the diluted pulp was about 500 ppm as CaCO<sub>3</sub> and the alkalinity was about 140 ppm as CaCO<sub>3</sub>. Additional NaHCO<sub>3</sub> was added to increase the pulp alkalinity to 340 ppm and 540 ppm as CaCO<sub>3</sub>. The pH was adjusted using hydrochloric acid to the range between 6.9 and 7.1. A cationic dry HMW polyacrylamide was used as the retention aid at 0.3 lb/ton followed by 1.0 lb/ton of colloidal silica. The order of addition of each chemical additive is strength resin and its promoter (60 sec), retention aid (15 sec) and silica (15 sec). The mixing times of each chemical additive are presented in parenthesis.

Handsheets (approximately 26 lb/1000ft<sup>2</sup> or 127 g/m<sup>2</sup> basis weight) were prepared according to the standard handsheet protocol by Dynamic Sheet Former (DSF). An aliquot of 3850 mL of diluted pulp was treated accordingly and then 250 mL was taken out for the measurement of zeta potential using the BTG SZP-06 zeta potential tester. The remaining furnish was used to make a sheet targeted at about 29-gm dry fibre using a DSF from Techpap. Sheets were pressed with a pneumatic roll press (set at 15 psi), drum-dried (set at 240 °F for 90-second total drying time), and post cured in a forced air oven for 5 minutes at 105 °C.

Before testing, the paper samples were conditioned at least overnight at 73 °F and 50 % relative humidity. This follows the TAPPI T 402 om-93, Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp hand sheet, and Related Products method.

## Test methods

### **Tensile Strength, Dry:**

5 Tensile strength is measured by applying a constant-rate-of-elongation to a sample and recording three tensile breaking properties of paper and paper board: the force per unit width required to break a specimen (tensile strength), the percentage elongation at break (stretch) and the energy absorbed per unit area of the specimen before breaking (tensile energy absorption). Only the dry tensile strength measurement is reported. This method is applicable to all types  
10 of paper, but not to corrugated board. This procedure references TAPPI Test Method T494. Eight measurements were taken per condition on CD and standard deviations were reported. A Thwing-Albert QC3A Series tensile tester was used for this study.

### **15 Tensile Strength, Immediate Wet:**

This test method is used to determine the wet tensile strength of paper and paperboard immediately after deionized water is brushed onto both sides of a paper sample. The wet tensile breaking strength is useful in the evaluation of the performance characteristics of tissue products, paper towels, bags and other  
20 papers subjected to stress during processing or use while wet. This method references TAPPI TEST Method T456. Eight measurements were taken per condition and averages were reported. A Thwing-Albert QC3A tensile tester was used.

### **25 Tensile Strength, 30 Minutes Soak**

Tensile strength is measured by wetting the sample strips in the deionized water for 30 minutes, removing excess water from the specimen, and then applying a constant-rate-of-elongation to a specimen and recording the force per unit width required to break a specimen. This is the tensile strength, which is the  
30 maximum tensile stress developed in the test specimen before rupture. This method is applicable most commonly on paper towel and paper board. This procedure references TAPPI Test Method T456. Eight measurements were taken per condition. A Thwing-Albert QC3A tensile tester was used.

Results:

In this invention UHMW GPAM was pre-blended with the partially crosslinking polyamidoamine epichlorohydrin as the booster technology. The dosage of conventional or UHMW GPAM is 8 lb/ton and the partially crosslinking polyamidoamine epichlorohydrin dosage is 4 lb/ton. Detailed results are shown in Figures 1 to 3 including the impact on CD dry tensile, CD Immediate wet tensile, CD 30 minutes soak tensile. Note that only mean values of each condition are reported.

This invention showed a significant improvement on both dry and wet strength development compared to UHMW GPAM used alone. This improvement was particularly significant for wet strength properties. Table 2 summarizes the percentage that the booster improved GPAM (at 8 lb/ton) performance at two different alkalinity levels (340 and 540 ppm as CaCO<sub>3</sub>).

Table 2. The impact of booster on GPAM performance.

| <b>Comparisons at certain alkalinity</b>                       | <b>CD Dry Tensile</b> | <b>CD Immediate Wet Tensile</b> | <b>CD 30 minutes soak</b> |
|--|-----------------------|---------------------------------|---------------------------|
| UHMW GPAM with booster at 340ppm vs. without booster at 140ppm | 1.5%                  | 7.3%                            | 19.6%                     |
| UHMW GPAM with booster at 340ppm vs. without booster at 340ppm | 1.3%                  | 18.9%                           | 19.4%                     |
| UHMW GPAM with booster at 540ppm vs. without booster at 140ppm | 5.8%                  | 10.8%                           | 20.9%                     |
| UHMW GPAM with booster at 540ppm vs. without booster at 540ppm | 4.7%                  | 26.5%                           | 24.8%                     |

Some other benefits are also presented in Figures 4 to 6.

Claims

1. A paper strength system for improving paper strength in manufacturing of paper or the like, wherein the paper strength system comprises
  - 5 - a structurally modified, water-soluble aldehyde functionalized 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, determined by gel permeation chromatography (GPC), and
  - a second polymer comprising amine groups or hydroxyl groups.
- 10 2. The paper strength system according to claim 1, wherein the second polymer is a cationic polymer.
3. The paper strength system according to claim 1 or 2, wherein the second  
15 polymer comprises primary and/or secondary amine groups.
4. The paper strength system according to any of the preceding claims, wherein the second polymer has a molecular weight in the range of 50 000 – 5 000 000 g/mol and preferably 100 000 - 2 000 000 g/mol.
- 20 5. The paper strength system according to any of the preceding claims, wherein the system comprises the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer in a weight ratio of 1:100 to 100:1, preferably in a weight ratio of 1:50 to 50:1, and preferably in a weight  
25 ratio of 1:10 to 10:1, as dry solids.
6. The paper strength system according to any of the preceding claims 3 to 5, wherein the second polymer comprising primary and/or secondary amine groups is selected from the group consisting of polyamine, polyamidoamine (PAA),  
30 polyamidoamine epihalohydrin (PAE), polyethyleneimine (PEI), polyvinylamine and any combination thereof, preferably the second polymer is polyamidoamine epihalohydrin (PAE).

7. The paper strength system according to claim 6, wherein the polymer is polyamidoamine epihalohydrin (PAE) having a molar ratio of epihalohydrin to amine in the range of 0.03:1.5, preferably 0.1:1.3, and more preferably 0.15:0.8.
- 5 8. The paper strength system according to any of the preceding claims, wherein a polydispersity index (Mw/Mn) of the structurally modified, water-soluble aldehyde functionalized polyacrylamide is < 5.0, preferably < 4.0 and more preferably < 3.5, determined by gel permeation chromatography (GPC).
- 10 9. The paper strength system according to any of the preceding claims, wherein the structurally modified, water-soluble aldehyde functionalized polyacrylamide is a glyoxylated polyacrylamide, preferably a glyoxylated cationic polyacrylamide.
- 15 10. The paper strength system according to any of the preceding claims, wherein the structurally modified, water-soluble aldehyde functionalized 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 1 M NaCl, at 25 °C and pH
- 20 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 a
- 25 polyaldehyde cross-linking agent to said aqueous medium for obtaining the aqueous composition of structurally modified water-soluble aldehyde functionalized polyacrylamide.
11. The paper strength system according to any of the preceding claims,
- 30 wherein solids content of an aqueous composition of the second polymer is at least 15 weight-%, preferably at least 20 weight-%
12. A process for manufacturing paper or the like comprising
- providing a fibre suspension,

- incorporating a paper strength system into the fibre suspension, which paper strength system comprises

5 (i) a structurally modified, water-soluble aldehyde functionalized 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, determined by gel permeation chromatography (GPC), and

(ii) a second polymer comprising amine groups or hydroxyl groups,  
and

- forming the fibre suspension into a fibrous web.

10

13. The process according to claim 12, wherein the second polymer is a cationic polymer.

14. The process according to claim 12 or 13, wherein the second polymer  
15 comprises primary and/or secondary amine groups.

15. The process according to any of the preceding claims 12 to 14, wherein the second polymer has a molecular weight in the range of 50 000 – 5 000 000 g/mol and preferably 100 000-2 000 000 g/mol.

20

16. The process according to any of the preceding claims 12 to 15, wherein the paper strength system comprises the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer in a weight ratio of 1:100 to 100:1, preferably in a weight ratio of 1:50 to 50:1, more preferably in  
25 a weight ratio of 1:10 to 10:1, as dry solids.

17. The process according to claim any of the preceding claims 14 to 16, wherein the second polymer comprising primary and/or secondary amine groups is selected from the group consisting of polyamine, polyamidoamine (PAA),  
30 polyamidoamine epihalohydrin (PAE), polyethyleneimine (PEI), polyvinylamine and any combination thereof, preferably the second polymer is polyamidoamine epihalohydrin (PAE).



18. The process according to claim 17, wherein the polymer is polyamidoamine epihalohydrin (PAE) having a molar ratio of epihalohydrin to amine in the range of 0.03:1.5, preferably 0.1:1.3 and more preferably 0.15:0.8.
- 5 19. The process according to any of the preceding claims 12 to 18, wherein an alkalinity of the fibre suspension is at least 100 ppm, preferably at least 200 ppm, calculated as  $\text{CaCO}_3$ .
- 10 20. The process according to any of the preceding claims 12 to 19, wherein the fibre suspension has a hardness of at least 100 ppm, preferably at least 200 ppm, more preferably at least 300 ppm, expressed as  $\text{CaCO}_3$ .
- 15 21. The process according to any of the preceding claims 12 to 20, wherein the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer are pre-mixed prior to the addition into the fibre suspension.
- 20 22. The process according to claim 21, wherein the premixed solution of the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer is diluted to at most 0.5 weight-%, preferably at most 0.1 weight-%, as dry solids prior to the addition to fibre suspension.
- 25 23. The process according to any of the preceding claims 21 or 22, wherein the premixed solution of the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer is added to the fibre suspension having a consistency of below 20 g/l.
- 30 24. The process according to any of the preceding claims 21 to 23, wherein the premixed solution of the structurally modified, water-soluble aldehyde functionalized polyacrylamide and the second polymer is added into the fibre suspension prior to a fan pump.
25. A paper product comprising the paper strength system according to any of the preceding claims 1 to 11 or manufactured by the process according to any of the preceding claims 12 to 24.

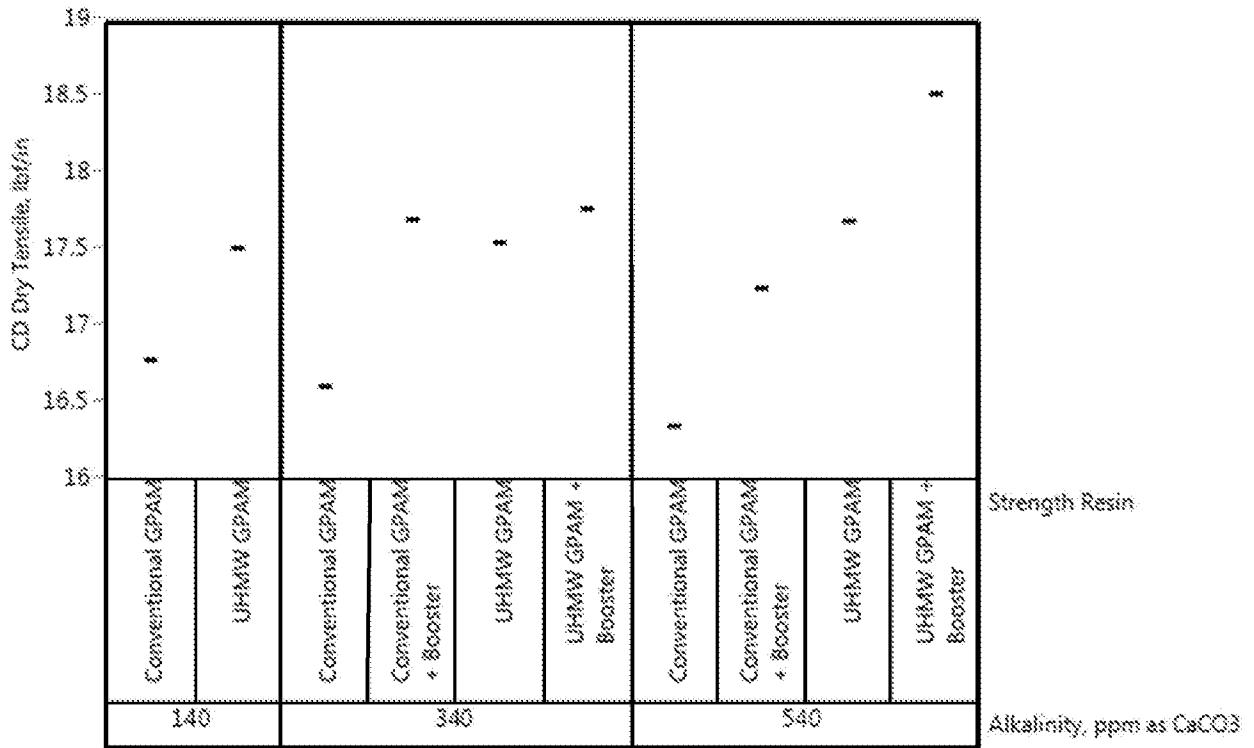


FIG. 1

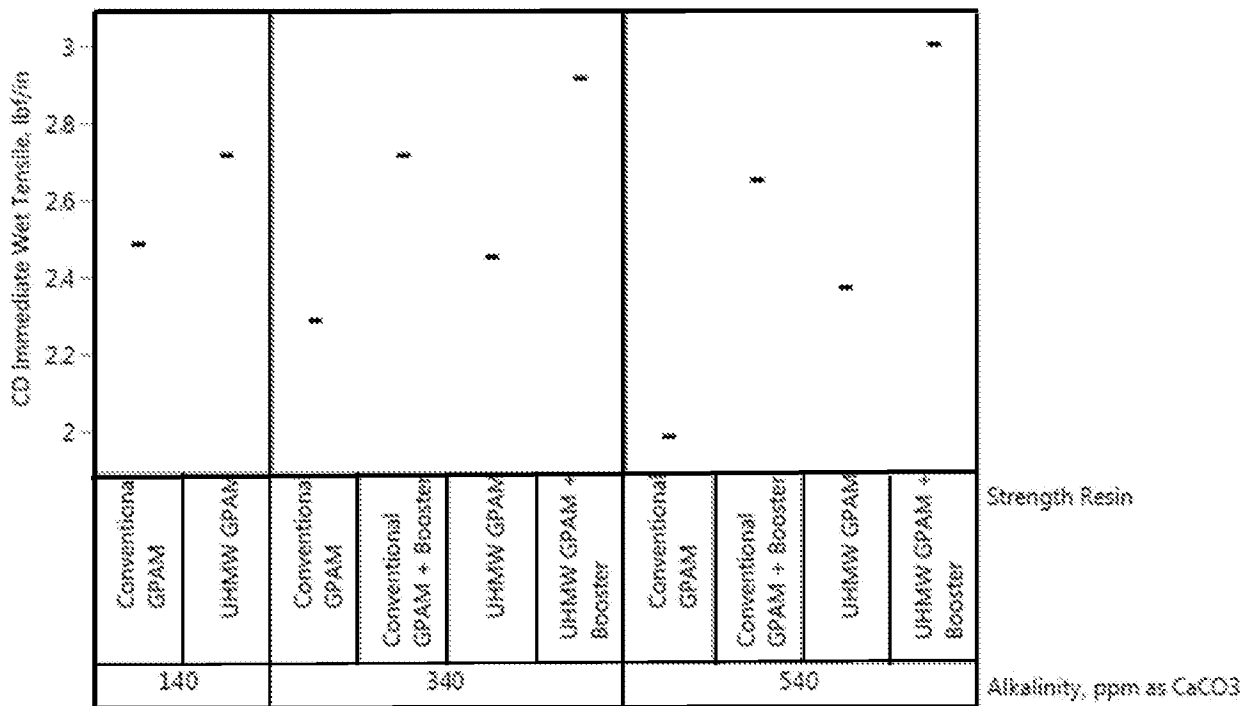


FIG. 2

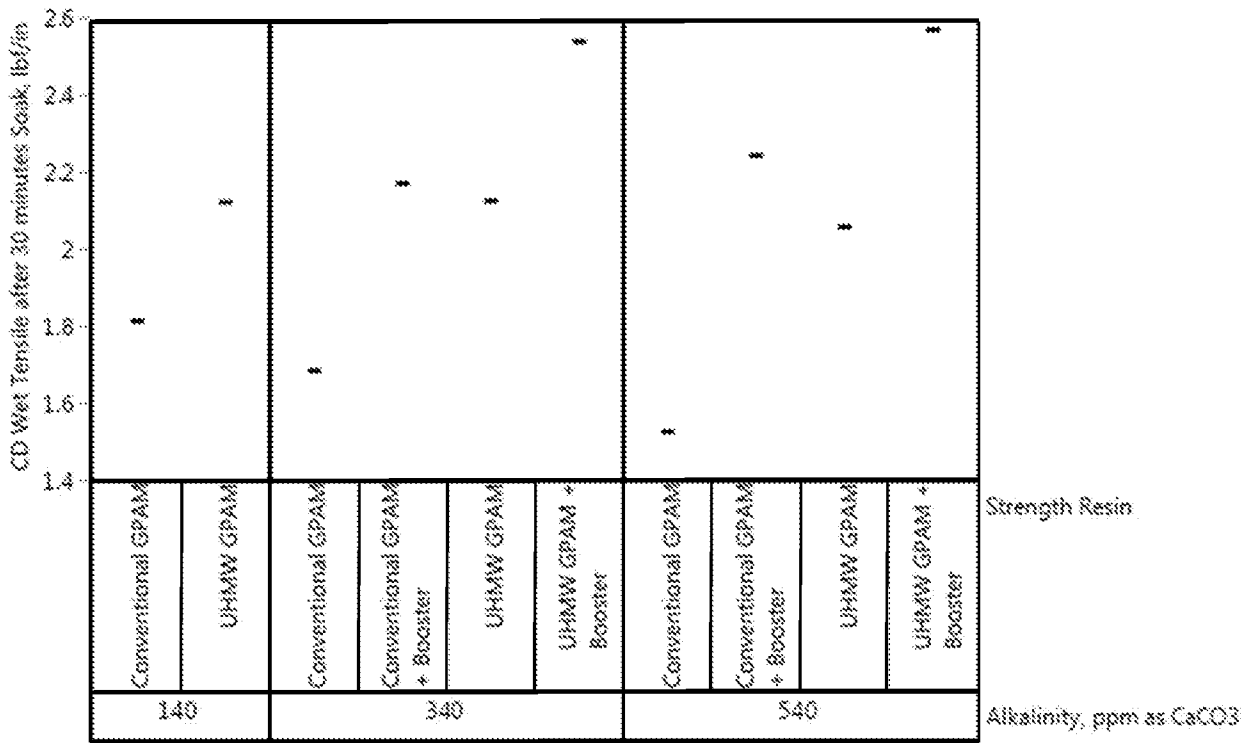


FIG. 3.

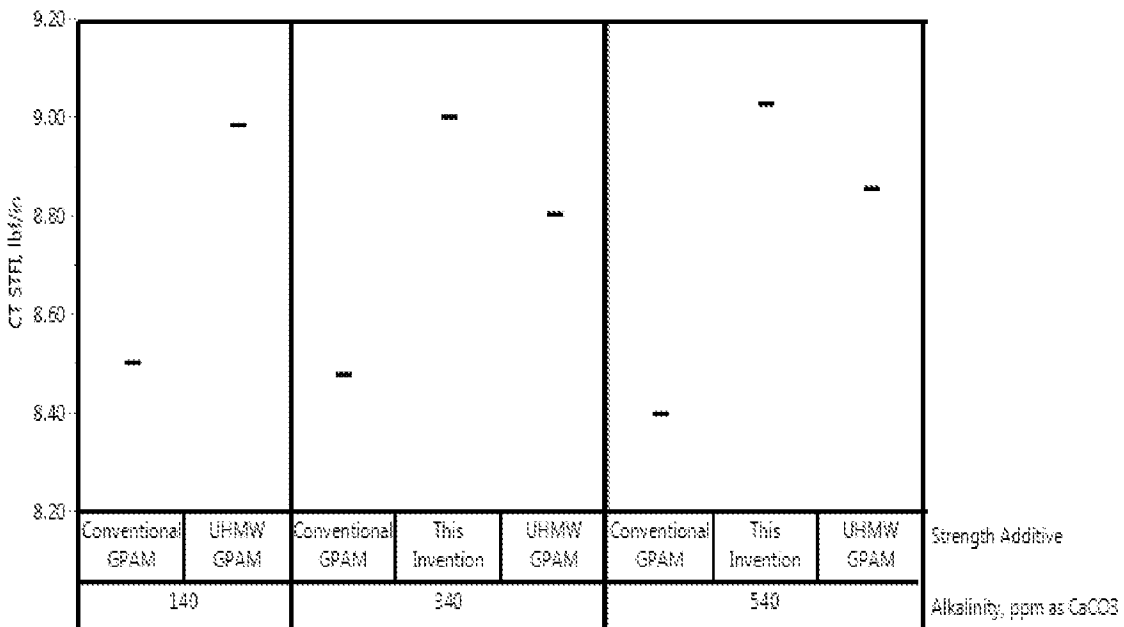


FIG. 4

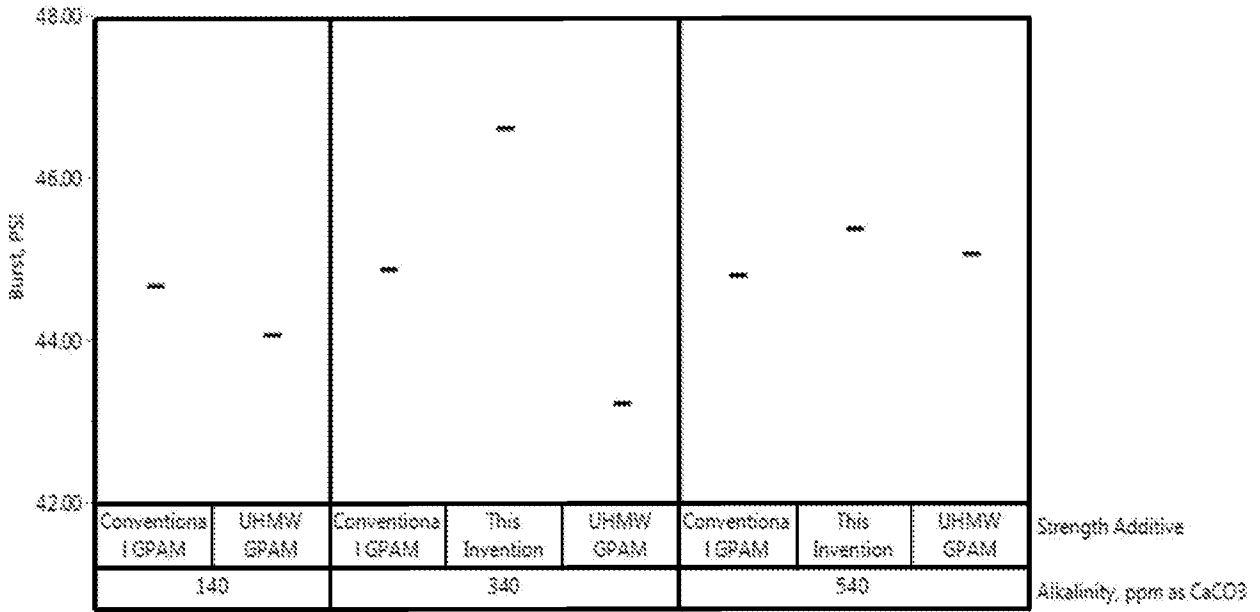


FIG.5

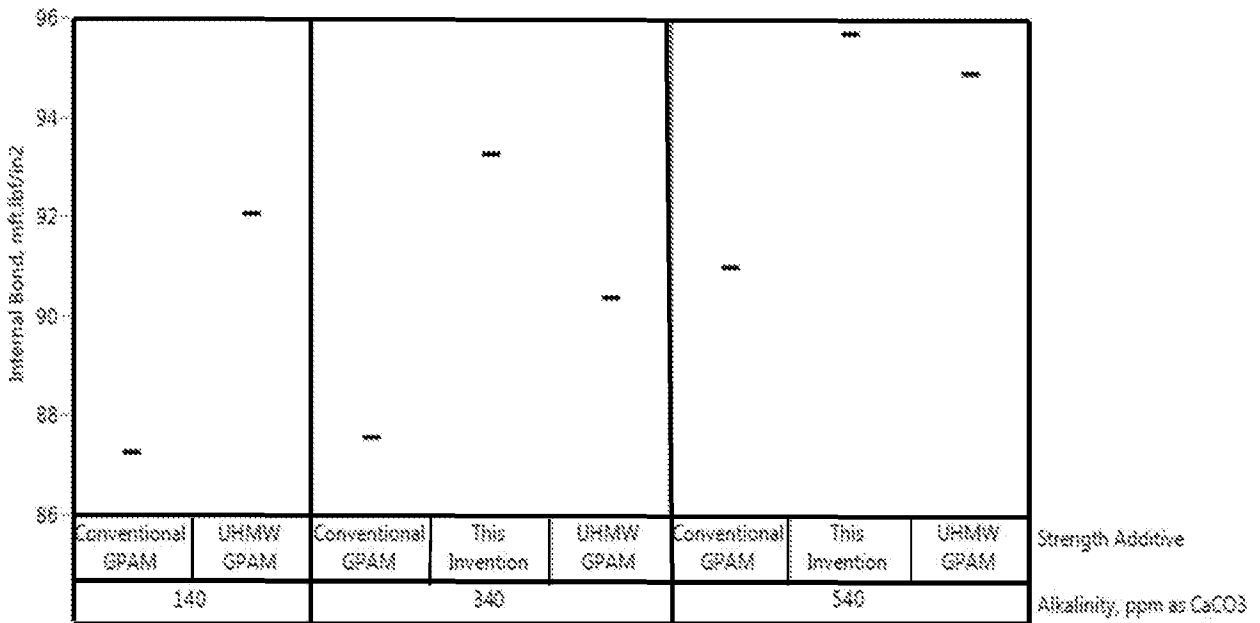


FIG.6

INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2016/063445

A. CLASSIFICATION OF SUBJECT MATTER  
INV. D21H17/37 D21H21/18 D21H21/20 D21H17/38  
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 |   |   |
|--|---|---|
| Category*                              | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.                             |
| X                                      | US 2016/222590 A1 (ZHU BO [CN] ET AL)<br>4 August 2016 (2016-08-04)<br><br>claims 1-25<br>paragraph [0050] - paragraph [0069]<br>-----  | 1-4,6,8,<br>9,12-15,<br>17,19,<br>20,22,<br>23,25 |
| X                                      | WO 2016/085836 A1 (ECOLAB USA INC [US])<br>2 June 2016 (2016-06-02)<br>page 4, line 5 - page 9, line 16<br>page 16, line 8 - line 10<br>claims 1-8; examples 1-7<br>-----<br><br>-/-- | 1-9,<br>11-25                                     |

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

|  |  |
|--|--|
| Date of the actual completion of the international search<br><br>2 June 2017   | Date of mailing of the international search report<br><br>14/06/2017 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br><br>Billet, Aina                               |

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2016/063445

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |   |  |
|--|---|--|
| Category*  | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.                                  |
| X  | WO 2016/170230 A1 (KEMIRA OYJ [FI])<br>27 October 2016 (2016-10-27)<br><br>page 6, line 6 - page 10, line 24<br>page 11, line 5 - line 13<br>claims 1-21; figures 2, 3; examples 3, 5,<br>8 | 1-4,6,8,<br>10,<br>12-15,<br>17,19,<br>20,22,<br>23,25 |
| A  | -----<br>US 5 401 810 A (JANSMA ROGER H [US] ET AL)<br>28 March 1995 (1995-03-28)<br>claims 1-13; examples 2, 6<br>-----  | 1-25   |

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Information on patent family members

International application No

PCT/US2016/063445

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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