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(54) Title: PAPER IMPROVING ADDITIVE

(57) Abstract: The invention relates to paper and paper products with new improved properties conferred by the use of additives made from water-soluble cationic polysaccharide graft copolymers, comprising a polymer backbone of at least one selected polysaccharide, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached. A favoured polysaccharide is starch. The additives allow for improved adsorption to the fibres use in said paper and paper products at the high conductivities present as a consequence of reduced or completely closed water circulation conditions, resulting in significantly improved end-properties in said paper and paper products.



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PAPER IMPROVING ADDITIVE

FIELD OF INVENTION

The present invention relates to the field of wet-end additives based on
5 modified polysaccharides used to improve end-properties in paper and paper products.

Specifically, the invention relates to paper and paper products with new improved properties conferred by the use of additives made from water-soluble cationic polysaccharide graft copolymers, comprising a polymer backbone of at
10 least one selected polysaccharide, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached. A favoured polysaccharide used in the invention is starch. The additives allow for improved adsorption to the fibres used in said paper and paper products, at the high conductivities present as a consequence of conditions of
15 reduced or completely closed water circulation, resulting in significantly improved end-properties in said paper and paper products.

BACKGROUND OF THE INVENTION

Starch has long been used commercially in the paper industry both as
20 retention and dry strength aid or additive, in paper production. Such additives are added to pulp as wet-end additives; i.e., the additives are added prior to sheet production, and are relatively effective in increasing the final dry strength of the resulting paper.

In US patent 4,744,864, Deets, et al. describes a method to obtain cationic
25 grafted starch copolymers comprising cationic starch, nonionic vinyl monomer and cationic monomer, to be used as cheaper and improved alternatives to water soluble polyacrylamides as dry strength additives for paper and paper products. Synthetic additives such as polyacrylamides suffer disadvantages such as higher cost and lower biodegradability; the incorporation of a natural polymer like starch both
30 decreases cost and improves the environmental aspects substantially.

Aldehyde-substituted acrylamidated starch polymers are other forms of modified cationic starches that have been described as wet strength additives [EP 0147 380]. A method to cationize granular starch by heterogeneous graft
copolymerization with cationic monomers, for example, 2-(methacryloyloxy)-
35 ethyl]-trimethylammonium chloride (TMAEMA), and a nonionic monomer, for example, acrylamide, was described by Gruber and Bothor [E. Gruber, R.Bothor, Starch/Stärke, vol. 50(6), pp. 257-264 (1998)].

Cellulose fibres used for paper making possess, in their natural form, anionic charges, while most cationic starch additives contain polyvalent cationic charges.

The performance of these additives, and subsequent end-properties in the products, such as increased dry tensile strength, z-strength and burst strength, are thought to be directly or indirectly dependent on the electrostatic interaction between the polyvalent cationic charges present on the additives and the anionic charges on the fibres.

An increasing trend today is to reduce fresh water consumption during paper manufacturing, which has led to efforts to close the water circuits at paper mills. This has led to an increasing concentration of dissolved and colloidal substances in the circulation water as well as an increase in the total electrolyte concentration, measurable as an increase in conductivity.

It has been observed that this increase, in its turn, negatively influences the adsorption of the cationic starch to the fibres, i.e., a lower saturation adsorption is achieved, since the polyelectrolyte interaction between cationic starch and the fibres is screened by a higher concentration of simple electrolytes. Added to this, an increase in microbiological activity is obtained, which further exacerbates the situation.

Thus, there is a need for an improved method or process, or a new additive, which could compensate for this decreased additive adsorption in reduced or completely closed water circulation conditions leading in its turn to diminished end-properties, such as burst strength and z-strength, in the resulting paper and paper products.

SUMMARY OF THE INVENTION

It has been found that by grafting cationic groups in a "cluster" onto starch backbone ("cluster cationization") instead of randomly grafting individual cationic groups onto starch backbone ("random cationization"), the adsorption of the starch onto cellulose fibres is less affected by increases in conductivity or electrolyte concentration. Therefore, cluster cationization is beneficial for enhancing adsorption of any cationic polymeric additive added to cellulose fibres in conditions of, for example, high conductivity as a consequence of reduced or completely closed water circulation, leading to improved paper and paper products made from these fibres.

The invention thus provides paper and paper products with improved properties at conditions where random cationized starch, as described above, is reduced in its efficiency to function, said improved properties being conferred by the use of additives made from water-soluble cationic starch graft copolymers, comprising a polymer backbone of starch, on which copolymers comprising one or more non-ionic monomer segments and one or more cationic monomer segments, are covalently attached. (The term "cluster cationic starch" or alternatively, "cluster

cationized starch", has been adopted herein as a simplified term to describe the above named family of graft copolymer additives based on the specific use of a starch backbone.) In conditions of, for example, high conductivity as a consequence of reduced or completely closed water circulation, cluster cationic starch additives
5 have been shown to manifest improved adsorption to the fibres used in the manufacture of said paper and paper products, resulting in the latter possessing significantly improved end-properties. These properties have been found to be better than normally achieved with standard cationic starch additives.

Although the use of starch as the selected polysaccharide is a favoured mode
10 in this invention, alternative polysaccharides may be used in the synthesis of said graft copolymer additives, especially those containing a hydroxymethyl group, for example, at the 6th-position of the monosaccharide unit. Such polysaccharides include for example, starch-type polysaccharides such as alpha-1,4 glucans, pullulan and other alpha-1,3-glucans, cellulose-type polysaccharides including beta-
15 1,4-glucans, and other beta-glucans including chitin, fructans, galacto- and gluco-mannans including guar, and xylocans.

Thus, according to another aspect, the invention provides paper and paper products with improved properties conferred by the use of "cluster cationic polysaccharides" made from water-soluble cationic polysaccharide graft
20 copolymers, comprising a polymer backbone of at least one selected polysaccharide, on which copolymers comprising one or more non-ionic monomer segments and one or more cationic monomer segments, are covalently attached.

Another objective of the present invention is a process or method for manufacturing new and improved paper and paper products comprising the use of
25 said cluster cationic polysaccharide additives.

The invention also provides in one specific case, a process or method for manufacturing new and improved paper and paper products comprising the use of said cluster cationic starch additives.

In another aspect, the invention provides new dry and wet strength additives,
30 namely, said cluster cationic polysaccharide additives, or in a more specific case, cluster cationic starch additives, which allow for improved adsorption to the fibres used in paper production, especially during production in conditions of, for example, high conductivity as a consequence of reduced or completely closed water circulation.

35 In a further aspect, the invention relates to cluster cationic polysaccharides, namely, said water-soluble polysaccharide graft copolymers comprising a polymer backbone of at least one selected polysaccharide, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached, wherein (a) said polysaccharide is present in

amounts from about 80 mole %, (b) said nonionic monomer is present in amounts from about 1 to 90 mole % of the block copolymer, (c) said cationic monomer is present in amounts from about 10 to 99 mole %, of the grafted portion of the copolymer additive.

- 5 The invention also provides in one specific case, cluster cationic starch, namely, water-soluble starch graft copolymers comprising a polymer backbone of starch, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached, wherein (a) said starch is present in amounts from about 80 mole %, (b) said nonionic monomer
10 is present in amounts from about 1 to 90 mole % of the block copolymer, (c) said cationic monomer is present in amounts from about 10 to 99 mole %, of the grafted portion of the copolymer additive.

- In a further aspect, the invention may be used as starch additives, after further derivatization with cellulose reactive groups, such as aldehyde and epoxide
15 groups, which react with cellulose after being adsorbed and are used to improve wet strength.

DESCRIPTION OF THE DRAWINGS

- The invention will be described in greater detail below, with reference to the
20 figures shown in the appended drawings, in which:

 Figure 1 shows that a significantly greater amount of cluster cationic starch is adsorbed, compared to standard cationic starch, at high conductivities.

 Figure 2 shows a schematic diagram of the Formett dynamic Sheetformer used.

- 25 Figure 3 shows that the increase or improvement in burst strength is more sustained with increasing conductivity, for the paper modified with "cluster cationic starch".

 Figure 4 shows that the increase in Z-strength is more sustained with increasing conductivity, for the paper modified with "cluster cationic starch".

- 30 Figure 5 shows that both the leachable metal ion (concentration) from the paper and conductivity in white water are significantly higher without effluent water.

 Figure 6 shows that conductivity increases with reduced effluent water.

35 DETAILED DESCRIPTION OF THE INVENTION

Definitions

 The term "cluster cationic starch", or alternatively, "cluster cationized starch" as used herein, refers to additives made from water-soluble cationic starch

graft copolymers, comprising a polymer backbone of starch, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached.

The term "cluster cationic polysaccharide(s)", or "cluster cationized polysaccharide(s)" as used herein, refers to additives made from water-soluble cationic polysaccharide graft copolymers, comprising a polymer backbone of at least one selected polysaccharide, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached.

The term "cluster cationization" as used herein, refers to the process of grafting copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, onto a polymer backbone comprising at least one selected polysaccharide. In the favoured mode, the polysaccharide used is starch.

The term "random cationization" as used herein, refers to the process of randomly grafting individual cationic groups onto a polymer backbone comprising at least one selected polysaccharide, or in one specific case, a starch backbone.

The term "traditional cationic starch", is used herein interchangeably with the term "standard cationic starch" (as used in fig.1 or in the claims), or simply, "cationic starch" (as used in fig.3 and 4).

The term "grafting" as used in this application refers to the process of covalently attaching a non-ionic, cationic or anionic copolymer by either (a) covalently attaching the copolymer by *in-situ* polymerization of a vinyl monomer or (b) covalently attaching a preformed copolymer to the starch or other suitable polysaccharide backbone.

The term "cluster" is intended in this application to mean a copolymer of a specific molecular weight range, attached or grafted on to a starch polymer backbone, comprising segments of cationic monomer segments, covalently bonded in linear fashion to nonionic monomer segments; each segment type possessing a specific average molecular weight range.

The terms "copolymer additive(s)", or "graft copolymer additive(s)" or "graft copolymer(s)" as used herein, all refer to the final graft-and-backbone structure of the copolymer as a whole, which is essentially the additive macromolecule.

The term "monomer segments" as used herein, may be interpreted to mean a polymer (if >1 monomer), or alternatively, the polymerized result of the relevant monomer molecule, possessing a specific molecular weight range.

The term "dry strength additive" as used herein, refers to an additive added during paper production, to increase or improve the final properties (for example, strength) of the paper.

The term "burst strength*" as used herein, refers to the resistance to an impact perpendicular to the plane as described by standard methods, DIN 53141, SCAN P24:99 and Tappi T807. (*The goals and details of these and other test methods for measuring strength properties of paper and paper products (with or without additives) are further discussed under the section "Detailed Description".)

The term "z-strength*" as used herein, refers to the strength measured in the thickness direction of the paper as described by standard methods, SCAN P80:98 and Tappi T541. (*The goals and details of these and other test methods for measuring strength properties of paper and paper products (with or without additives) are further discussed under the section "Detailed Description".)

The term "fibres" used in this application and to which the "cluster cationic starch" additive is intended to be used on, includes all fibres employed in the production of tissue and containerboard paper, including pulp fibres from chemical pulp, chemo-mechanical pulp and/or chemo-thermo mechanical pulp (CTMP) and recycled fibres.

Other types of fibres used for enhancing properties such as strength, absorption or softness of the paper, for example, those made from regenerated cellulose or synthetic material such as polyolefin, polyesters, polyamides etc., are also meant to be included in the term "fibres" as used in this application.

The term "tissue paper" is intended to include all types of tissue paper, including the types described in the following paragraphs:

Tissue paper emerging from the tissue machine as a single-ply paper sheet, which may then be converted to the final tissue product in many different ways, for example, by being embossed, laminated to a multi-ply product, rolled or folded.

Tissue paper comprising one or more layers. In the case of more than one layer, this layering is accomplished either in a multi-layered headbox, by forming a new layer on top of an already formed layer or by couching together already formed layers. These layers cannot, or only with considerable difficulty, be separated from each other and are joined mainly by hydrogen bonds. The different layers may be identical or may have different properties with respect to, for example, fibre composition and chemical composition. Physical properties which are important for tissue and towel paper includes softness, both bulk and surface softness and thickness (bulk). Tensile properties (strength, stretch-at-break, energy absorption and stiffness) are also very important, both in dry and wet conditions. Absorption rate and capacity, including liquid spreading, as well as the ability to hold liquid especially when compressed are also important physical properties.

Laminated multi-ply tissue products comprise at least two tissue plies, which are often joined by either adhesive or mechanically. The adhesive may be applied all over the paper or just in regions, for example dots or lines, or only along the edges of the product. The mechanical methods of joining mainly include

5 embossing; either over the entire area of the plies or only along the edges, termed "edge embossing". In the final product the plies are mostly easily detectable and can often be separated from each other as single plies.

The term "containerboard products" refers to liner and fluting (corrugated medium) products with basis weights ranging from 70 to 440 g/m² produced from

10 recycled fibre material, from chemo-thermo mechanical pulp (CTMP) or from chemical pulp (also combinations thereof). Containerboard is the raw material when producing corrugated board, the fluting (corrugated medium) being the wavy layer placed in between and separating two flat layers of papers, the liners. Some type of glue is also used to adhere the different layers. Multiple layer corrugated board is

15 produced when additional corrugated medium and liner layer is added to the initial structure. Containerboard paper may as such comprise one or more layers. In the case of more than one layer, this layering is accomplished by forming a new layer on top of an already formed layer or by couching together already formed layers. These layers cannot, or only with considerable difficulty, be separated from each

20 other and are joined mainly by hydrogen bonds. The different layers may be identical or may have different properties regarding, for example, fibre composition and chemical composition. White-top testliner is an example of a two layer structure with one brown/gray and one high brightness layer. Containerboard, being the raw materials for producing corrugated board, can be pressed intensively to high sheet

25 density to give high in-plane strength. Extended nip pressing is therefore widely spread within this sector. The paper is, when based on recovered paper, usually treated with native starch in a sizepress and then dried again to further improve strength properties. The size press has very important drawbacks since it is the production bottleneck on many containerboard machines and for the increase in

30 energy consumption due to the fact that the paper has to be dried twice, before and after the size press, instead of just once. This is the reason why most mills struggle to use wet-end starch, which is particularly difficult in this type of machines, as the containerboard mills together with cardboard and some tissue mills have reached the highest degrees of water closure in the paper industry. Several mills in Europe

35 are completely closed; for example, they are only introducing water to the process to make up for the steam loss during drying.

Detailed description of the invention

The invention relates to paper and paper products with new improved properties conferred by the use of additives made from water-soluble cationic polysaccharide graft copolymers, comprising a polymer backbone of at least one
5 selected polysaccharide, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached. These additives are referred to as "cluster cationic polysaccharides" in this application.

The various paper and paper products to which this invention relates to
10 include all types of tissue paper, as defined earlier.

The various paper and paper products to which this invention also relates to include all types of containerboard products, both liner and corrugated medium (fluting) as defined earlier.

A favoured polysaccharide used in the invention is starch.

15 It was observed that by grafting cationic groups in a "cluster" onto the backbone of starch additives ("cluster cationization") instead of randomly grafting individual cationic groups onto starch backbone ("random cationization"), the adsorption of said starch additives onto cellulose fibres is less affected by increases in conductivity or electrolyte concentration. The observed improved adsorption
20 occurs at conditions of high conductivity, from about 3000 $\mu\text{S}/\text{cm}$, such as from about 4000 $\mu\text{S}/\text{cm}$, such as from about 5000 $\mu\text{S}/\text{cm}$.

These conditions are found, for example, as a consequence of reduced or completely closed water circulation. "Cluster cationic starch" additives were found to manifest improved adsorption to the fibres used in the manufacture of said paper
25 and paper products, resulting in the latter possessing significantly improved end-properties. These end-properties have been found to be better than normally achieved with traditional cationic starch additives.

The end-properties of the paper and paper products are most clearly reflected in their strength properties. For example, the in-plane and out-of-plane strength
30 properties are important parameters for assessing the quality of containerboard. Paper is essentially a 2-dimensional material and in-plane strength refers to strength measurements in this plane while out-of-plane strength measurement refers to measurements perpendicular to this plane. Both in- and out-of-plane properties are measured in tensile and compression modes. The complexity of this assessment has
35 led to the use and development of various related methods measure these properties. For example, in-plane compressive strength is measured using the Short span compression test, SCT (ISO 9895) or the Ring crush test, RCT (SCAN P-34). The assessment of in-plane tensile strength involves measurement of various tensile properties (strength, stretch-at-break, energy absorption and stiffness, using

standard methods such as ISO 1924 and SCAN P-67). The assessment of out-of-plane strength on paper involves measurement of burst strength (using, for example, standard methods such as ISO 2759 and SCAN P-24). For corrugated board, the corrugated medium test, CMT (ISO 7263), and the corrugated crush test CCT (SCAN P-42) are used. Out-of-plane tensile strength properties are measured on the paper using methods including Ply bond (TUM 403), Scott Bond (Tappi T-569), Z-strength (SCAN P-80), Z-directional toughness (SCAN P-90) and Pick resistance (Tappi T-459).

Accordingly, it is believed that cluster cationization is beneficial for enhancing adsorption of any cationic polymeric additive added to cellulose fibres at the high conductivities present as a consequence of reduced or completely closed water circulation systems, leading to improved paper and paper products made from these fibres.

In the modified paper and paper products treated with the copolymer additives described herein, an increase/improvement (over products using traditional or standard cationic starch additives, at the high conductivities present as a consequence of reduced or completely closed water circulation conditions) in burst strength from about 0.1 to about 0.4 MN/kg, such as from about 0.2 to about 0.3 MN/kg was observed.

An increase/improvement (over products using standard cationic starch additives at the high conductivities present as a consequence of reduced or completely closed water circulation conditions) in the Z-strength from about 20 kN/m², such as from about 40 kN/m², and such as from about 60 kN/m², was also observed.

The term "cluster cationic starch" is used herein to describe a specific case of cluster cationic polysaccharides, namely, water-soluble cationic starch graft copolymers, comprising a polymer backbone of starch, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached.

The starch used may be derivatized with other functional groups, for example aldehyde and epoxide groups, to improve the wet strength. The starch used may be selected from the group consisting of potato, corn, wheat and tapioca starch.

More specifically, the starch polymer used as the backbone polymer is a granular alpha-(1-4) linked glucan, consisting of two components; amylose, which is linear with a Mw from 200,000 to 700,000 g/mole (See A.H. Young, 'Fractionation of Starch', in 'Starch Chemistry and Technology', R.L. Whistler, J.N. BeMiller and E.F. Paschall (Eds.), Academic Press Inc., London, 1984), and amylopectin, which is highly branched, possessing a Mw from 10 to 500 million (same reference above), depending on the starch source.

The total amount of monomer units of the starch included in the copolymer additives, range from about 80 to about 99 mole %, such as from about 95 to about 99 mole %, of the copolymer additive.

Additionally, the starch is present in amounts from about 0.2 to about 10 wt%, such as between from about 1 to about 5 wt%, such as from about 2 to about 4 wt% of the finished paper product.

The starch used in the additives may also be replaced with other polysaccharides especially those containing a hydroxymethyl group, covalently attached at one or more of the positions of the monosaccharide unit; for example, at the 6th-position of the monosaccharide unit. Such polysaccharides include for example, starch-type polysaccharides such as alpha-1,4 glucans, pullulan and other alpha-1,3-glucans, cellulose-type polysaccharides including beta-1,4-glucans, and other beta-glucans including chitin, fructans, galacto- and gluco-mannans including guar, and xylocans.

The copolymer additive comprises a selected polysaccharide backbone on which copolymers comprising one or more cationic monomer segments and one or more non-ionic monomer segments are grafted.

The grafted segments together form the "cluster", as referred to in "cluster cationic polysaccharides", or in one specific case, "cluster cationic starch". One section of this grafted copolymer (the segment comprising cationic polymer, originating from the cationic monomer) is positively charged, whereas the other section of the same grafted copolymer (i.e, the segment comprising nonionic polymer, originating from the nonionic or anionic monomer) is uncharged and /or negatively charged. Effectively therefore, in cluster cationized starch, highly charged regions interspersed between uncharged regions are now present on the starch molecules. The net charge on the additive is, however, positive (cationic).

As opposed to normal or random cationization reactions, where cationic groups are created on or grafted to, and randomly distributed over the polymer network, cluster cationization results in the grafting of cationic and non-ionic monomer segments in an ordered block or "cluster". During grafting reactions at least two possible modes of reaction are thought to be possible: (a) the non-ionic, cationic or anionic monomers are grafted directly and simultaneously polymerized *in-situ* to result in copolymer clusters on the polysaccharide backbone; (b) an assembly (or polymerization) of the non-ionic, cationic or anionic monomers occur prior to the grafting reaction, forming a copolymer, which is then covalently attached onto the polysaccharide backbone.

As previously described, the block copolymer is the grafted entity. The grafted portion of the copolymer additive possesses a weight average molecular

weight range of from about 500 to about 20000 g/mol, such as from about 800 to 15000 g/mol, 1000 to 10000 g/mol.

Also, the amount of grafted portion in the additive range from about 1 to about 20 mole %, such as from about 3 to about 18 mole %, such as from about 5 to 15 mole %, of the total graft polymer additive.

The grafted portion of the copolymer additive possesses a cationic charge density of from about 0.5 to about 10 milliequivalents/g; such as from about 1.5 to about 9 milliequivalents/g; such as from about 2.5 to about 7.5 milliequivalents/g.

It should be noted, however, that the copolymer additive itself possesses a lower cationic charge density of from about 0.05 to about 1 milliequivalents/g; such as from about 0.1 to about 0.8 milliequivalents/g; such as from about 0.15 to about 0.6 milliequivalents/g.

The grafted portion of the copolymer additive comprises from about 5 to about 50 cationic monomer segments, each of average weight from about 160 to about 240 g/mole, and from about 1 to about 50 nonionic monomer segments, each of average molecular weight from about 50 to about 100 g/mole.

Within the grafted portion of the copolymer additive, the cationic monomer is selected from the group comprising methyl chloride tertiary or quaternary salts of dimethylaminoethyl methacrylate, and methyl chloride tertiary or quaternary salts of methyl diallyl amine and dimethyl sulfate tertiary or quaternary salts of dimethylaminoethyl methacrylate.

Other reactants may include trimethyleaminoethyleacrylate, trimethyleaminomethyleacrylate, trimethyleaminopropylemethacrylamide, or 3-acrylamide-3-methylebutyletrimethyleammoniumchloride, plus mannich modified polyacrylamide (PAM).

The cationic monomer segment(s) within the grafted portion of the graft copolymer additive, is present in amounts from about 10 to about 99 mole %, such as from about 20 to about 80 mole %, of the grafted portion.

Within the grafted portion of the copolymer additive, the nonionic monomer is a vinyl monomer, such as acrylamide.

The total amount of nonionic monomer, such as acrylamide, included in the copolymer additive should generally be in the ranges typically from about 1 to about 90 mole %, such as from about 1 to about 18 mole %, such as from about 1 to about 17 mole %, such as from about 1 to about 15 mole %, of the grafted portion of the copolymer additive.

Within the grafted portion of the copolymer additive, as part of the "non-ionic" segment, an anionic monomer can also be incorporated, selected from the group comprising acrylic acids.

The total amount of anionic monomer included in the copolymer additives range from about 0 to about 6 mole %, such as from about 0 to 4 mole %, such as from about 0 to about 2 mole %, of the grafted portion of the copolymer additive.

In contrast to the cluster cationic starch additives used in this invention,
5 modified cationic starches traditionally used in paper manufacturing have most often the cationic charges more or less randomly distributed on the polymer backbone.

It is further believed that the use of cluster cationic starch additives has the effect of increasing the *local* cationic charge density, i.e., present on the cationic
10 parts of the grafted copolymer, without changing the average cationic charge in the starch.

As a result, the required electrostatic interaction between these polyvalent cationic charges present on the additives and the anionic charges on the fibres are now allowed to occur undisturbed by the increased total electrolyte concentration in
15 the circulation water. At the same time, the adsorption saturation levels would not be affected since the polyvalent cation charges would now be dispersed through the backbone at suitable intervals between uncharged regions in such a way that the same average cationic charge density is obtained. The underlying mechanism for such an effect has been discussed by Wågberg and Kolar [Ber. Bunsenges. Phys.
20 Chem., vol. 100(6), pp. 984-993 (1996)] and van de Steeg, et al. [H.G.M. van de Steeg, et al., Langmuir, vol. 8, pp. 2538-2546 (1992)]. The underlying mechanism for improved adsorption at elevated ionic strength with the cationic charges in clusters has been discussed by Wågberg [Nordic Pulp Paper Res. J., vol. (15)5, pp 586-597 (2000)].

25 The synthesis of this additive has been described by Gruber and Bothor [E. Gruber, R.Bothor, Starch/Stärke, vol. 50(6), pp. 257-264 (1998)]. However, some modifications to the method described were made, to further increase the level of substitution. For example, the cationization reaction was repeated a second time on the same substrate. This is described in detail in the experimental section in
30 Example 1.

The invention also relates to a process or method for manufacturing new and improved paper and paper products possessing better end-product properties than normally achieved with standard cationic starches, comprising the use of said cluster cationic polysaccharide additives. The invention also provides a process or
35 method for manufacturing new and improved paper and paper products at the high conductivities present as a consequence of reduced or completely closed water circulation conditions comprising the use of said cluster cationized starch additives.

In a further aspect, the invention relates to cluster cationic polysaccharides, namely, water-soluble polysaccharide graft copolymers comprising a polymer backbone of at least one selected polysaccharide, on which copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, are covalently attached, wherein (a) said polysaccharide is present in amounts from about 80 mole % of the copolymer additive, (b) said nonionic monomer is present in amounts from about 1 to 90 mole % of the grafted portion of the copolymer additive, (c) said cationic monomer is present in amounts from about 10 to 99 mole % of the grafted portion of the copolymer additive.

The invention also provides cluster cationic starch, namely, water-soluble starch graft copolymers comprising a polymer backbone of starch, onto which block copolymers comprising one or more nonionic monomer segments and one or more cationic monomer segments, have been grafted, wherein (a) said starch is present in amounts from about 80 mole % of the copolymer additive, (b) said nonionic monomer is present in amounts from about 1 to 90 mole % of the grafted portion of the copolymer additive, (c) said cationic monomer is present in amounts from about 10 to 99 mole % of the grafted portion of the copolymer additive.

In a further aspect, the invention may be used as starch additives, after further derivatization with any cellulose reactive groups, including aldehyde and epoxide groups, which react with cellulose after being adsorbed and are used to improve wet strength.

Furthermore, use of the invention allows new applications for the paper and paper products modified with polysaccharide, more specifically, starch based additives.

EXAMPLES

Examples 1- 4 given below illustrate the invention. These examples are present to exemplify the invention; they are not, however, intended to limit in any way the invention as covered by the claims.

Example 1

Objective

The aim of this experiment was to show that cluster cationized starch adsorbs better to fibres used in paper production at high conductivities than does traditional cationic starch.

Experimental

(i) Materials

(a) *Cluster cationized starch: Synthesis method*

5 The cluster cationic starch used was prepared by *in-situ* polymerization of [2-(metacryloyloxy-ethyl)]-trimethylammoniumchloride (TMAEMA) onto uncooked starch according to a procedure described by Gruber et al. [Starch/Stärke, vol. 50, pp. 257-264 (1998)]. In the original method, the chemical activation of the starch (or "cationization") required to initiate the grafting reaction was achieved using
10 ceric ammonium nitrate.

 In this invention, 2 equivalents (or molar ratio) cerium, or an excess of cerium ions, was used. Furthermore, in order to reach a higher level of substitution, the cationization reaction was repeated a second time on the same substrate (now with 1 equivalent cerium). A free radical is then expected to be formed at the C₂
15 atom of the glucopyranose unit in the starch backbone. This radical is then the polymer initiation site for the grafting and polymerization reactions for the cationic monomer, TMAEMA and non ionic monomer, ACM. The starch was finally cooked prior to use.

20 (b) *Standard cationic starch*

 The standard cationic starch used for comparison was Pearlbond 903, obtained from Lyckeby Stärkelsen, Sweden.

(ii) Test methods

25 (a) *Measurement of charge density*

 The cationic charge density of both starches was determined prior to the adsorption experiments by polyelectrolyte titration described by Wågberg et al. [Nord Pulp Paper Res. J., vol. 4(2), p. 71 (1989)]. Potassium polyvinylsulphate was used as the anionic titrant and the point of charge neutralization was measured with
30 a streaming current detector described by Bley [Paper Technology, April (1992)]. The measured charge density was 0.15 µ-equivalents/g for both the cluster cationic starches and for the reference starch.

(b) *Adsorption*

35 The adsorption experiments were performed according to the method used by Wågberg and Kolar, [Ber. Bunsenges. Phys. Chem., vol.100(6), pp. 984-993 (1996)].

Results and Conclusions

Figure 1 shows the adsorbed concentrations (mg/g) of cluster cationic starch and standard cationic starch vs. the measured starch charge (meq./g). It is clear from figure 1 that a significantly greater amount of cluster cationized starch is adsorbed to fibres, compared to standard cationic starch, at high conductivities. The electrolyte concentration, obtained with sodium chloride and measured as conductivity, used in this experiment was 5,6 mS/cm. (This conductivity value corresponds to a typical situation in a recycled fibre mill.

10 Example 2

Objective

The aim of this experiment was to show that paper produced using fibres modified with cluster cationic starch show greater burst strength than when using fibres modified with standard cationic starch, at conditions of high conductivity.

15

Experimental

(i) Materials and equipment

Paper with a basis weight of 150 g/m² was produced with a Formette Dynamic sheetformer. The equipment, which is schematically illustrated in Figure 2, comprises at least one furnish container (1) with a mixer, a pump (2), connected to the furnish container (1), a pressure compensation vessel (3), connected to the pump (2) and a rotating vertically standing drum (4). In the drum (4) is a tubular wire (5) placed co-axially with the drum so that water can flow from the inner side of the wire (5) to the outer side. Within the drum there is also a nozzle (6) that moves up and down. The nozzle (6) is connected to pressure compensation vessel (3). The nozzle pressure is adjusted with pressurised air (7) that is added to the pressure compensation vessel (3).

(ii) Procedure

The fibres to be used were disintegrated at 80 °C for 4 minutes with a pilot disintegrator. A sufficient amount of fibres for the sheet to be produced was mixed with water in the furnish container until a fibre concentration of 5.0 g/l. The conductivity was adjusted to the desired value by adding a 50/50 weight-% NaCl/CaCl₂ (powder). With this treatment the pH value read was about 7.0 ± 0.2 without adjustment. If there were any preferred paper additives they were thereafter added to the furnish.

The circulation of the drum was started (1200 r/minute) and water was sprayed onto the brass wire so that a water film was evolved on the wire. The furnish pump was started and nozzle moves up and down and sprays the furnish

onto the wire until the furnish container was empty. The sheet was dewatered on the rotating drum for about a minute until no more water was removed. The wire with the wet paper web was then taken out of the drum and placed on a blotting paper. The wire was removed and another blotting paper was placed on the other side of the wet paper web. The paper web and the blotting paper was then pressed in a cylinder press one time at 3 bars pressure. The paper was loosened from the blotting papers and clamped in a frame and dried in 150°C for 10 minutes.

(iii) Test methods

10 (a) *Burst strength*

The paper was subjected to 24 hours of conditioning at 23 °C, 50 % relative humidity (RH) before testing; the paper properties were also tested in at the same conditions. Basis weight (mass of a unit area of paper, expressed as grams per square meter (g/m^2)), thickness and density were measured and evaluated according to standard method SCAN-C 28:76. Burst strength was measured according to SCAN-P 24:77 (DIN 53141).

(b) *Conductivity*

The conductivity was measured by submerging a HANNA Instrument HI 8733 conductivity meter into the furnish container.

Results

Table 1

Conductivity ($\mu\text{S/cm}$)	Increase in burst strength (%), Cationic starch	Increase in burst strength (%), Cluster-cationized starch
500	20.1	22.6
5000	0.6	11.2
10000	0.0	11.8

Conclusions

Both table 1 and figure 3, the latter of which shows the burst strength (MN/kg) vs. conductivity ($\mu\text{S/cm}$), indicate that the increase in burst strength is more sustained with increasing conductivity, for the paper produced using fibres modified with cluster cationized starch, compared with fibres modified with standard cationic starch.

Example 3

Objective

- The aim of this experiment was to show that paper produced using fibres
5 modified with cluster cationized starch show greater Z-strength than when using
fibres modified with standard cationic starch at conditions of high conductivity.

Experimental

(i) Materials and equipment

- Paper with a basis weight of 150 g/m² was produced with a Formette
10 Dynamic sheetformer (see Figure 2). The equipment comprises at least one furnish
container (1) with a mixer, a pump (2), connected to the furnish container (1), a
pressure compensation vessel (3), connected to the pump (2) and a rotating
vertically standing drum (4). In the drum (4) is a tubular wire (5) placed co-axially
with the drum so that water can flow from the inner side of the wire (5) to the outer
15 side. Within the drum there is also a nozzle (6) that moves up and down. The nozzle
(6) is connected to pressure compensation vessel (3). The nozzle pressure is
adjusted with pressurised air (7) that is added to the pressure compensation vessel
(3).

- The fibres to be used were disintegrated at 80 °C for 4 minutes with a pilot
20 desintegrator. A sufficient amount of fibres for the sheet to be produced was mixed
with water in the furnish container until a fibre concentration of 5.0 g/l. The
conductivity was adjusted to the desired value by adding a 50/50 weight %
NaCl/CaCl₂ (powder). The pH was found to be with this treatment about 7.0 ± 0.2
without adjustment. If there were any preferred paper additives they were thereafter
25 added to the furnish.

- The circulation of the drum was started (1200 r/minute) and water was
sprayed onto the brass wire so that a water film was evolved on the wire. The
furnish pump was started and nozzle moves up and down and sprays the furnish
onto the wire until the furnish container was empty. The sheet was dewatered on the
30 rotating drum for about a minute until no more water was removed. The wire with
the wet paper web was then taken out of the drum and placed on a blotting paper.
The wire was removed and another blotting paper was placed on the other side of
the wet paper web. The paper web and the blotting paper was then pressed in a
cylinder press one time at 3 bars pressure. The paper was loosened from the blotting
35 papers and clamped in a frame and dried in 150°C for 10 minutes.

(ii) Test methods

(b) Z-strength

The paper was subjected to 24 hours of conditioning at 23 °C, 50 % relative humidity (RH) before testing; the paper properties were also tested at the same conditions. Grammage, thickness and density was measured and evaluated according to standard method SCAN-C 28:76. Z-strength (strength in the thickness direction of the paper) was evaluated according to SCAN-P 80:98.

(b) Conductivity

Conductivity was measured by submerging a HANNA Instrument HI 8733 Conductivity meter into the furnish container.

*Results***Table 2**

Conductivity ($\mu\text{S}/\text{cm}$)	Increase in Z- strength (%)	Increase in Z- strength (%)
	Cationic starch	Cluster-cationized starch
500	15.5	17.9
5000	2.6	10.0
10000	3.1	8.1

Conclusions

Both table 2 and figure 4, the latter of which shows the Z-strength (kN/m^2) vs. conductivity ($\mu\text{S}/\text{cm}$), indicate that the increase in Z-strength is more sustained with increasing conductivity, for the paper produced using fibres modified with cluster cationized starch, compared with fibres modified with standard cationic starch.

Example 425 *Objective*

The aim of this experiment was to display that the values of metal ion concentration measured in the water extract from paper produced at various paper mill locations reflect the ion concentration in the white water system.

30 *Experimental*

In this example, the metal concentration in white water in various paper mills were measured. ("White water" refers to paper-mill water clouded by suspended

fibres and paper additives, typically draining from forming wires, thickeners, save-alls, or grinders.) This data is shown in Table 3.

The various paper mills have different degrees of closure of the white water system. The mills in Argovia and Djursland have completely closed white water systems, resulting in no waste water being released to the effluent. Some water is, however, lost through evaporation and is subsequently replaced. The paper mills at De Hoop and Lucca have partly closed white water systems and emit about 5 kg water / kg of produced paper (note that 1 ton(ne) equals 1000 kg).

Samples were taken from the paper mills and were prepared according to the method SS-EN 647. After filtration through a 0.45 µm Millipore filter, the metal content (including Al, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Md, Na and Zn) was measured with an inductive plasma instrument according to ISO 11885. As can be observed in figure 4, paper mills with closed white water systems show a higher metal ion concentration in the extract from paper, compared to the paper mills with partly closed white water systems.

Results and Conclusions

Table 3

	Argovia	Djursland	Lucca	De Hoop
Effluent water (m ³ /T)	0	0	5	4.5
Aluminium (mg/kg)	10.7	400	354	313
Boron (mg/kg)	41.0	51.0	20.1	11.1
Barium (mg/kg)	2.18	0.85	0.57	2.25
Calcium (mg/kg)	3610	2710	1350	2040
Copper (mg/kg)	<0.1	<0.10	<0.10	<0.10
Iron (mg/kg)	2.85	2.11	0.56	5.43
Potassium (mg/kg)	149	159	91.4	62.4
Magnesium (mg/kg)	23.5	83.1	59.6	27.8
Manganese (mg/kg)	0.54	1.52	1.50	0.76

Molybdenum (mg/kg)	<0.05	<0.05	<0.05	<0.05
Sodium (mg/kg)	1850	2560	1160	499
Phosphorus (mg/kg)	Not applicable or not available (NA)	NA	NA	NA
Silicon (mg/kg)	NA	NA	NA	NA
Zinc (mg/kg)	0.65	0.16	1.39	<0.02
Sulphur (mg/kg)	NA	NA	NA	NA
Total metal ion conc., (mg/kg)	5609	5829	2864	2852
Only sodium and calcium (mg/kg)	5460	5270	2510	2539

Figure 5 shows the leachable metal ion concentration (mg/kg) and conductivity ($\mu\text{S}/\text{cm}$) with and without effluent water. The figure indicates that both the leachable metal ion concentration and conductivity are significantly higher without effluent water.

Figure 6, which shows the conductivity ($\mu\text{S}/\text{cm}$) vs. effluent water (m^3/T) in containerboard mills, substantiates this trend, since conductivity is shown to decrease with increasing volume of effluent water.

The results also indicate that the metal content extractable from a paper sample may be used as a measure of the metal content in the water containment area, i.e., where the paper originates from. These values may be used to characterize the paper product(s).

CLAIMS

1. Paper and paper products comprising copolymer additives wherein said additives are made from water-soluble cationic polysaccharide graft copolymers,
5 comprising a polymer backbone of at least one selected polysaccharide, on which copolymers comprising one or more non-ionic vinyl monomer segments and one or more cationic monomer segments, are covalently attached.
2. Paper and paper products according to claim 1, wherein said additives
10 manifest improved adsorption to the fibres employed in the manufacture of said paper and paper products.
3. Paper and paper products according to any one of the preceding claims, wherein said improved adsorption occurs at conditions of high conductivity, from
15 about 3000 $\mu\text{S}/\text{cm}$, such as from about 4000 $\mu\text{S}/\text{cm}$, such as from about 5000 $\mu\text{S}/\text{cm}$.
4. Paper and paper products according to any one of the preceding claims, wherein said products possess an increase/improvement in burst strength, over
20 products employing standard cationic starch, from about 0.1 MN/kg to about 0.4 MN/kg, such as from about 0.2 MN/kg to about 0.3 MN/kg.
5. Paper and paper products according to any one of the preceding claims, wherein said products possess an increase/improvement in Z-strength, over
25 products employing standard cationic starch, from about 20 kN/m^2 , such as from about 40 kN/m^2 and such as from about 60 kN/m^2 .
6. Paper and paper products according to any one of the preceding claims, wherein the one or more selected polysaccharide(s) comprise starch, and/or other
30 polysaccharides containing a hydroxymethyl group covalently attached at one or more of the positions of the monosaccharide unit, selected from the group consisting of starch-type polysaccharides such as alpha-1,4 glucans, pullulan and other alpha-1,3-glucans, cellulose-type polysaccharides including beta-1,4-glucans, and other beta-glucans including chitin, fructans, galacto- and gluco-mannans
35 including guar, and xylocans.
7. Paper and paper products according to claim 6, wherein said polysaccharide is starch.

8. Paper and paper products according to claim 7, wherein said starch is selected from the group consisting of potato, corn, wheat and tapioca starch.
9. Paper and paper products according to any one of claims 7-8, wherein said
5 starch is a granular alpha-(1-4) linked glucan, consisting of two components; amylose, which is linear with a Mw from 200,000 to 700,000 g/mole, and amylopectin, which is highly branched, possessing a Mw from 10 to 500 million, depending on the starch source.
- 10 10. Paper and paper products according to any one of claims 7-9, wherein said starch is present in amounts ranging from about 80 to about 99 mole %, such as from about 95 to about 99 mole %, of the copolymer additive.
11. Paper and paper products according to any one of claims 7-10, wherein said
15 starch is present in amounts ranging from about 0.2 to about 10 wt%, such as from about 1 to about 5 wt%, such as from about 2 to about 4 wt% of the finished paper product.
12. Paper and paper products according to any one of the preceding claims,
20 wherein the grafted portion of the copolymer additive possesses a weight average molecular weight range of from about 500 to about 20000 g/mol, such as from about 800 to 15000 g/mol, 1000 to 10000 g/mol.
13. Paper and paper products according to any one of the preceding claims,
25 wherein said grafted portion of the copolymer additive is present in amounts ranging from about 1 to about 20 mole %, such as from about 3 to about 18 mole %, such as from about 5 to 15 mole %, of the copolymer additive.
14. Paper and paper products according to any one of the preceding claims,
30 wherein said grafted portion of the copolymer additive possesses a cationic charge density ranging from about 0.5 to about 10 milliequivalents/g, such as from about 1.5 to about 9 milliequivalents/g, such as from about 2.5 to about 7.5 milliequivalents/g.
- 35 15. Paper and paper products according to any one of the preceding claims, wherein said copolymer additive possesses a cationic charge density of from about 0.05 to about 1 milliequivalents/g; such as from about 0.1 to about 0.8 milliequivalents/g; such as from about 0.15 to about 0.6 milliequivalents/g.

16. Paper and paper products according to any one of the preceding claims, wherein said grafted portion of the copolymer additive comprises from about 5 to about 50 cationic monomer segments, each of average weight from about 160 to about 240 g/mole, and from about 1 to about 50 nonionic monomer segments, each of average molecular weight from about 50 to about 100 g/mole.
17. Paper and paper products according to any one of the preceding claims, wherein said cationic monomer segment(s) within the grafted portion of the graft copolymer additive, is selected from the group comprising methyl chloride tertiary or quaternary salt(s) of dimethylaminoethyl methacrylate, and methyl chloride tertiary or quaternary salt(s) of methyl diallyl amine and dimethyl sulfate tertiary or quaternary salt(s) of dimethylaminoethyl methacrylate, trimethyleaminoethyleacrylate, trimethyleaminomethyleacrylate, trimethyleaminopropylemethacrylamide, or 3-acrylamide-3-methylebutyletrimethyleammoniumchloride, and mannich modified polyacrylamide.
18. Paper and paper products according to any one of the preceding claims, wherein said cationic monomer segment(s) within the grafted portion of the copolymer additive, is present in amounts from about 10 to about 99 mole %, such as from about 20 to about 80 mole %, of said grafted portion.
19. Paper and paper products according to any one of the preceding claims, wherein said nonionic monomer segment(s) within the grafted portion of the copolymer additive, is a vinyl monomer.
20. Paper and paper products according to claim 19, wherein said vinyl monomer is acrylamide.
21. Paper and paper products according to any one of the preceding claims, wherein said nonionic monomer segment(s) is present in the grafted portion of the copolymer additive in amounts from about 1 to about 90 mole %.
22. Paper and paper products according to any one of the preceding claims, wherein the paper comprises a water leachable potassium concentration from about 100 mg/kg ($\pm 5\%$), such as from about 120 mg/kg ($\pm 5\%$), such as from about 140 mg/kg ($\pm 5\%$).

23. Paper and paper products according to any one of the preceding claims, wherein the paper comprises a water leachable sodium concentration from about 1200 mg/kg ($\pm 5\%$), such as from about 1400 mg/kg ($\pm 5\%$), such as from about 1600 mg/kg ($\pm 5\%$).

5

24. Paper and paper products according to any one of the preceding claims, wherein the paper comprises a water leachable sodium and calcium concentration from about 3000 mg/kg ($\pm 5\%$), such as from about 4000 mg/kg ($\pm 5\%$), such as from about 5000 mg/kg ($\pm 5\%$).

10

25. Paper and paper products according to any one of the preceding claims, wherein said paper and paper products comprise a water leachable total metal concentration from about 3000 mg/kg ($\pm 5\%$), such as from about 4000 mg/kg ($\pm 5\%$), such as from about 5000 mg/kg ($\pm 5\%$).

15

26. Process for manufacturing paper and paper products according to any one of the preceding claims, comprising use of said copolymer additives.

27. Dry/wet strength additives used in said paper or paper and paper products according to any one of the preceding claims 1-25, wherein said additives are made from water-soluble cationic polysaccharide graft copolymers, comprising a polymer backbone of at least one selected polysaccharide, on which copolymers comprising one or more non-ionic vinyl monomer segments and one or more cationic monomer segments, are covalently attached.

25

28. Dry/wet strength additives according to claim 27, wherein (a) said polysaccharide is present in amounts from about 80 mole % of the copolymer additive, (b) said nonionic monomer is present in amounts from about 1 to 90 mole % of the grafted portion of the copolymer additive, (c) said cationic monomer is present in amounts from about 10 to about 99 mole % of the grafted portion of the copolymer additive.

30

35

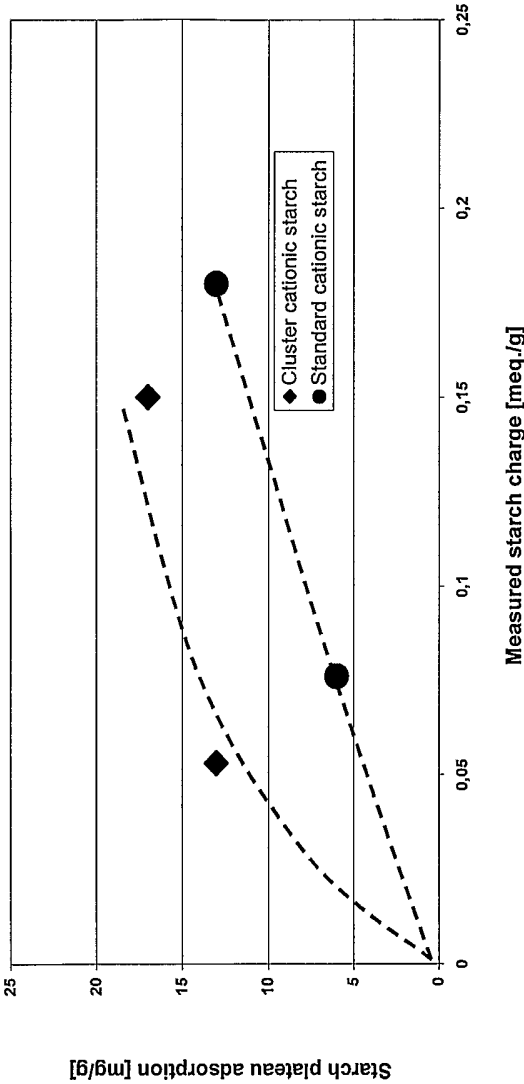


Figure 1

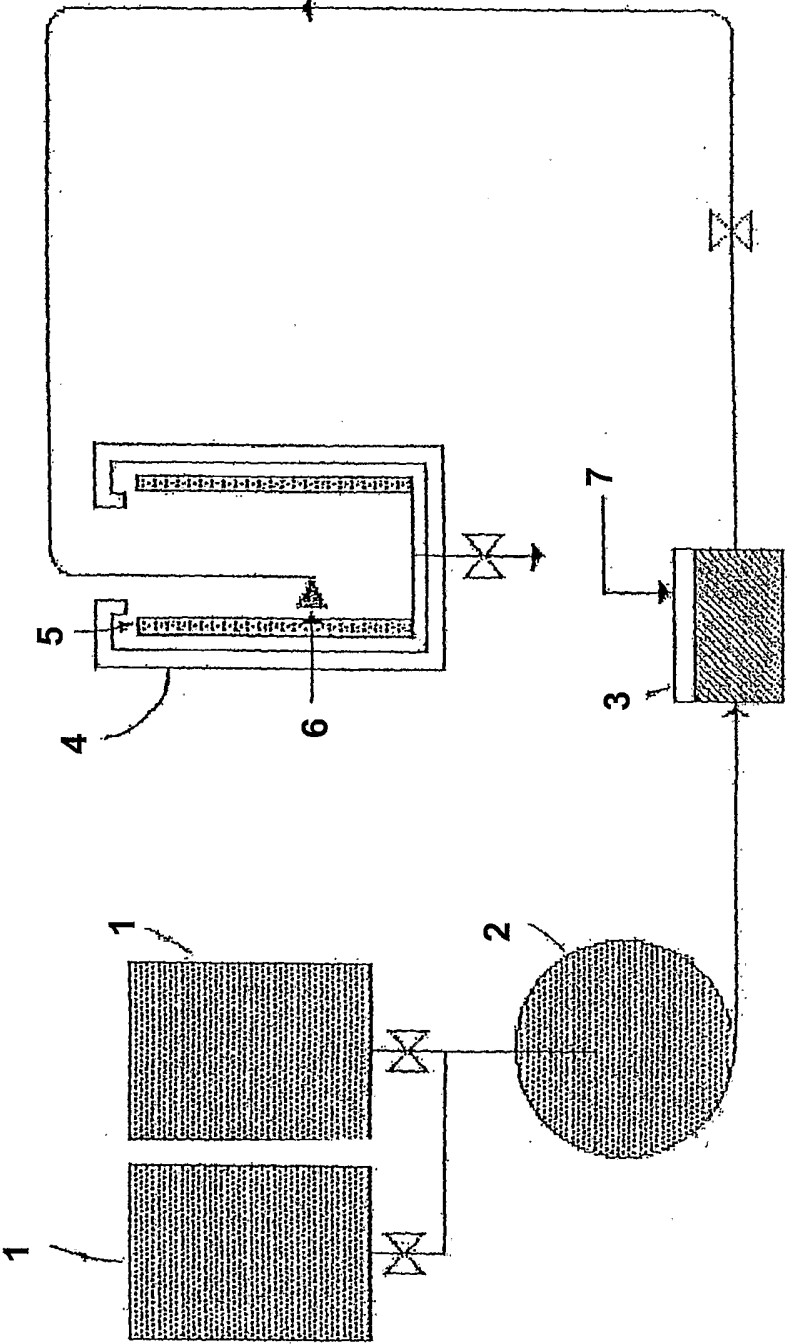


Figure 2

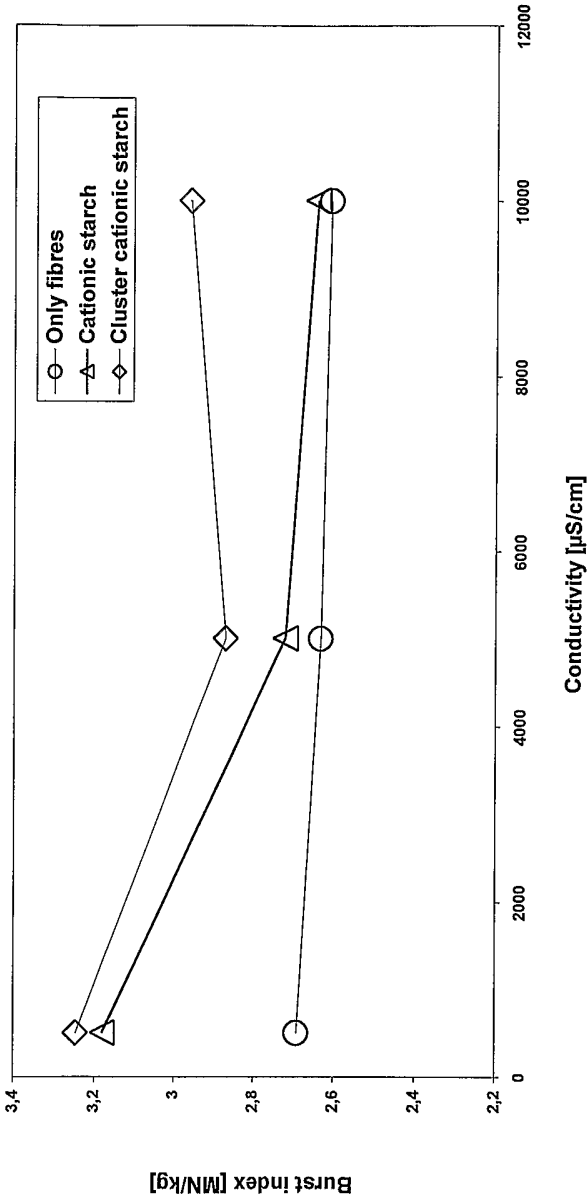


Figure 3

Figure 4

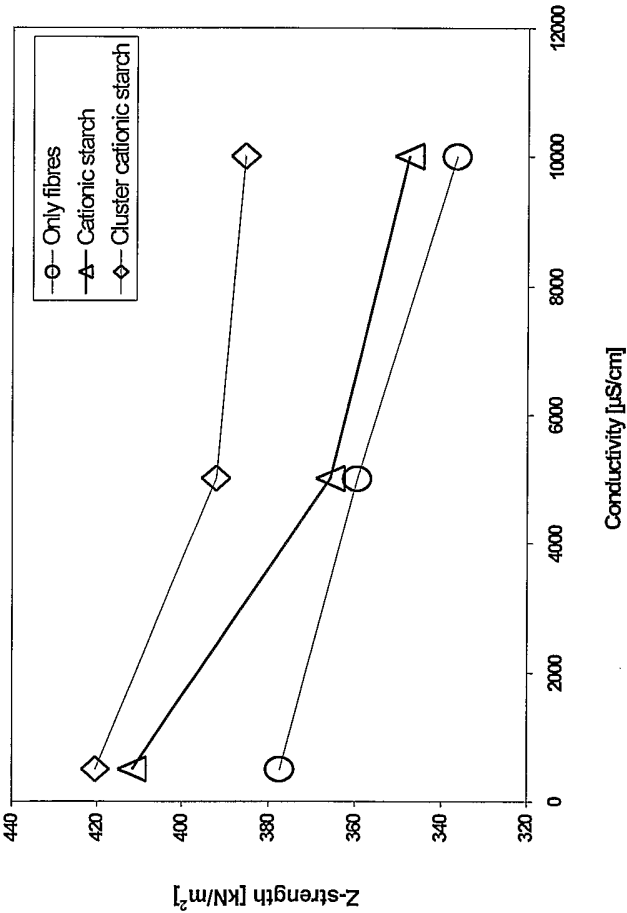


Figure 5

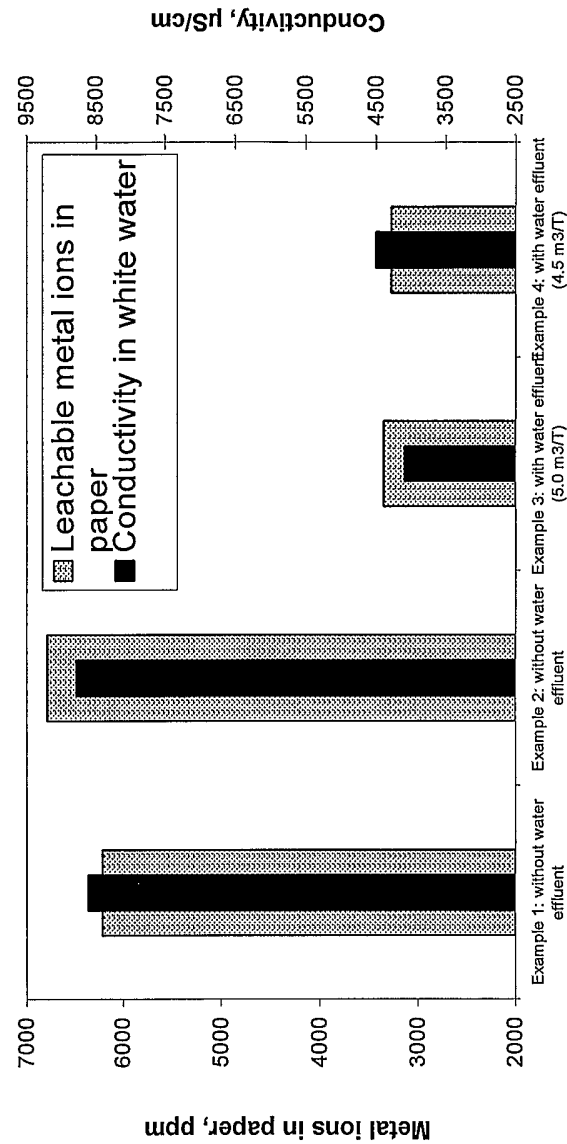
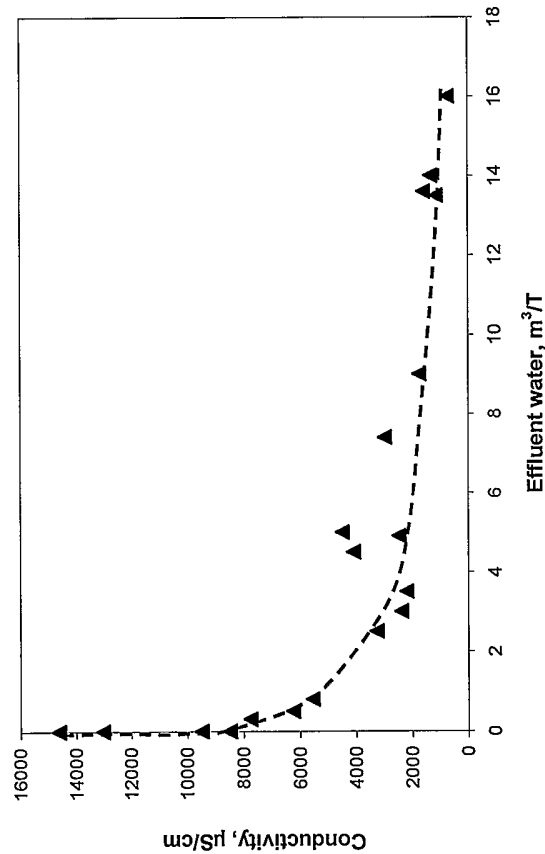


Figure 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 2004/001392

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08F 251/00, D21H 17/24, D21H 17/28, C08B 31/00

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)

IPC7: D21H, C08F, C08B

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

SE,DK,FI,NO classes as above

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

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GRUBER ERICH ET AL, "Cationisation of Starch Granules by Graft Copolymerisation", Starch/Stärke 1998, Vol. 50, No. 6, p 257-264, ISSN:0038-0606, --	1-28
A	EP 0147380 A2 (MONSANTO COMPANY), 3 July 1985 (03.07.1985) --	1-28
A	US 4744864 A (GARY L. DEETS ET AL), 17 May 1988 (17.05.1988) --	1-28

☒ 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

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

4 May 2005

Date of mailing of the international search report

11-05-2005

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 2004/001392

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WÄGBERG LARS ET AL, "Adsorption of Cationic Starch on Fibres from Mechanical Pulps", Berichte der Bunsen - Gesellschaft Physical chemistry chemical physics 1996, Vol. 100, No. 6, p. 984-993, ISSN:0005-9021 --	1-28
A	WÄGBERG LARS ET AL, "Polyelectrolyte adsorption onto cellulose fibres - A review", Nordic Pulp and Paper Research Journal 2000, Vol. 15, No. 5, p. 586-597 -- -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/04/2005

International application No.

PCT/SE 2004/001392

EP	0147380	A2	03/07/1985	SE	0147380	T3	
				AT	46200	T	15/09/1989
				AU	571914	B	28/04/1988
				AU	3669584	A	20/06/1985
				BR	8406417	A	08/10/1985
				CA	1254316	A	16/05/1989
				DE	3479677	D	00/00/0000
				ES	538562	A	16/01/1986
				ES	8604266	A	01/06/1986
				FI	844956	A	17/06/1985
				JP	60147421	A	03/08/1985
				KR	8601054	B	01/08/1986
				NO	166370	B,C	02/04/1991
				NO	845051	A	17/06/1985
				NZ	210561	A	30/03/1988

US	4744864	A	17/05/1988	AU	5439786	A	18/09/1986
				BR	8601022	A	18/11/1986
				CA	1254315	A	16/05/1989
				EP	0194987	A	17/09/1986
				ES	552857	A	01/11/1987
				ES	8800309	A	01/01/1988
				FI	860982	A	12/09/1986
				JP	61211319	A	19/09/1986
				NO	860889	A	12/09/1986
				NZ	215416	A	29/09/1988
				US	4684708	A	04/08/1987
