

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

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

12 December 2024 (12.12.2024)



(10) International Publication Number

WO 2024/252066 A1

(51) International Patent Classification:

D21H 17/24 (2006.01) D21H 27/10 (2006.01)

D21H 21/18 (2006.01)

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

— of inventorship (Rule 4.17(iv))

(21) International Application Number:

PCT/FI2024/050289

Published:

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

(22) International Filing Date:

04 June 2024 (04.06.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/471,545 07 June 2023 (07.06.2023) US

20235962 08 August 2023 (08.08.2023) FI

(71) Applicant: KEMIRA OYJ [FI/FI]; Energiakatu 4, 00180 Helsinki (FI).

(72) Inventors: HIETANIEMI, Matti; c/o Kemira Oyj, P.O. Box 44, 02271 Espoo (FI). KORHONEN, Markus; c/o Kemira Oyj, P.O. Box 44, 02271 Espoo (FI). KARPPI, Asko; c/o Kemira Oyj, P.O. Box 44, 02271 Espoo (FI). KONN, Jonas; c/o Kemira Oyj, P.O. Box 44, 02271 Espoo (FI). BEHABTU, Natnael; Monza (IT). ADELMAN, Douglas; c/o Nutrition & Biosciences USA 4, Inc., 3490 Winton Place, Rochester, New York 14623 (US).

(74) Agent: PAPULA OY; P.O. Box 981, 00101 Helsinki (FI).

(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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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, ME, 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: STRENGTH AGENT FOR PAPER, BOARD, OR THE LIKE

(57) Abstract: The present invention relates to a paper, board, or the like, strength agent, comprising cationic alpha-1,3-glucan, a paper, board, or the like, product comprising the strength agent and a method for making the product.

WO 2024/252066 A1

STRENGTH AGENT FOR PAPER, BOARD, OR THE LIKE**FIELD OF THE INVENTION**

The present invention relates to a paper,
5 board, or the like, strength agent. The present invention also relates to a paper, board, or the like, product comprising the strength agent and a method for making the product.

10 BACKGROUND OF THE INVENTION

In the manufacture of virgin and recycled paper or board, the properties of the fibre stock as well as the final paper or board are modified by adding various chemicals to the fibre stock before the formation of the
15 paper or board web. Synthetic cationic polymers and starches are commonly used in papermaking to increase, for example, the dry strength properties of the final paper or board. The cationic polymers and starches are added to the fibre stock where they interact with the
20 components of the stock, e.g. fibres and/or fillers.

An issue with the synthetic cationic polymers is that they are not biocompatible and thus an environmental hazard. Additionally, synthetic cationic polymers are expensive. Finally, they are prepared as well
25 as stored as a solution, which is challenging logistically.

In view of the ecological impact of manufacturing polymers and the on-going discussion of the possible harmful environmental effects of the extensive polymer usage, there is a need for alternative solutions. There is a growing desire to reduce the use of fully synthetic chemicals also in paper and board making
30 and to further improve the environmental aspects and sustainability of cellulosic products by using chemicals
35

and additives based on natural substances, which preferably are even biodegradable.

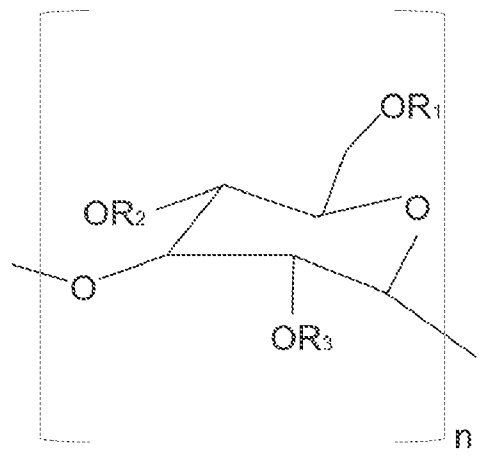
5 Starches are undesirable because they do not perform well especially in recycled fibre based corrugated board wet-end applications. Thus, these are not extensively used.

10 There is an increasing demand for paper and board, especially for corrugated board. The paper and board should have good strength properties, especially a good SCT index, CMT30 index and burst index.

15 As such there is a need for strength agents that overcome the drawbacks of conventional strength agents while still providing a good SCT index, CMT30 index and burst index.

SUMMARY

20 According to a first aspect of the invention, a paper, board, or the like, strength agent, comprising cationic alpha-1,3-glucan, wherein the cationic alpha-1,3-glucan is water soluble, wherein the cationic alpha-1,3-glucan is represented by the structure,



25

wherein R_1 , R_2 and R_3 are independently H or a positively charged organic group, wherein the cationic alpha-1,3-

glucan has a molecular weight of 350 000 to 1 500 000 g/mol calculated by PEO calibrated SEC, and wherein the cationic alpha-1,3-glucan has a degree of cationic substitution of 0.15 to 0.5, is provided.

5

According to a second aspect of the invention, a paper, board, or the like, product comprising the paper, board, or the like, strength agent according to the first aspect of the invention is provided.

10

According to a third aspect of the invention, a method for making a paper, board, or the like, product comprising,

15

- i) providing a fibre stock,
- ii) adding the paper, board, or the like, strength agent according to the first aspect of the invention to the fibre stock,
- iii) forming a fibrous wet web,
- 20 iv) optionally, wet pressing and/or drying the web, and
- v) optionally, subjecting the web to size press treatment,

25 is provided.

DETAILED DESCRIPTION

It is obvious to a person skilled in the art that with the advancement of technology, the basic idea of the invention may be implemented in various ways. The invention and its embodiments are thus not limited to the examples described below, instead they may vary within the scope of the claims.

35

Strength agent

According to a first aspect of the invention, a paper, board, or the like, strength agent, comprising cationic alpha-1,3-glucan, wherein the cationic alpha-1,3-glucan is water soluble, is provided.

5

The cationic alpha-1,3-glucan of the paper, board, or the like, strength agent according to the first aspect of the invention may have a degree of cationic substitution of 0.15 to 0.5, or 0.15 to 0.35, or
10 0.17 to 0.25.

The degree of cationic substitution defines how many substituted groups are contained in the cationic alpha-1,3-glucan, calculated per one anhydroglucose
15 unit of the cationic alpha-1,3-glucan. The degree of substitution of cationic alpha-1,3-glucan, which is cationized with 2,3-epoxypropyltrimethyl-ammonium chloride, is typically calculated by using the nitrogen content of pure dry cationic alpha-1,3-glucan, which does not
20 contain any other nitrogen sources than the quaternary ammonium groups. The nitrogen content is typically determined by using the commonly known Kjeldahl-method, e.g. according to ISO 1871:2009. The degree of substitution of cationic alpha-1,3-glucan, which is cationized
25 with 2,3-epoxypropyltrimethylammonium chloride may be calculated by using the following equation:

$$DS = (162 \times N\%) / (1400 - (N\% \times 151.6)),$$

30 where 162 is the molecular weight of an anhydroglucose unit (AHG), N-% is the nitrogen value in %, 1400 is the molecular weight of nitrogen multiplied by 100 and 151.5 is the molecular weight of 2,3-epoxypropyltrimethylammonium chloride.

35

The cationic alpha-1,3-glucan of the paper, board, or the like, strength agent according to the

first aspect of the invention may have a solubility of at least 90 wt.-%, or at least 95 wt.-%, or at least 98 wt.-% in water at a temperature of 22 °C.

5 The cationic alpha-1,3-glucan is considered to be water soluble when 1 g cationic alpha-1,3-glucan is dissolved at a pH of 4-9 and in room temperature (e.g. 20-25 °C) in 230 ml water and when filtered through a 100 micron cloth, no insoluble cationic alpha-1,3-glucan
10 is detected on the filter (less than 1% of dry solid matter remains on the filter).

 A cationic alpha-1,3-glucan or derivative thereof that is "insoluble", "aqueous-insoluble", "wa-
15 ter-insoluble" (and like terms) herein does not dissolve (or does not appreciably dissolve) in water or other aqueous conditions, optionally where the aqueous conditions are at a pH of 4 to 9 (e.g., pH 6 to 8) and/or temperature of about 1 to 130 °C (e.g., 20 to 25 °C). In
20 some aspects, less than 1.0 gram (e.g., no detectable amount) of an aqueous-insoluble cationic alpha-1,3-glucan or derivative thereof dissolves in 1000 ml of such aqueous conditions (e.g., water at 23 °C).

25 The inventors have surprisingly found that the aforementioned degrees of substitution in cationic alpha-1,3-glucan result in sufficient water solubilities for applications requiring water solubility. However, these degrees of substitution do not exceed values that
30 would be harmful for the environment. The aforementioned degrees of substitution have been found to provide the optimal balance between performance, the cost of production and environmental aspects.

35 The cationic alpha-1,3-glucan of the paper, board, or the like, strength agent according to the first aspect of the invention may have a molecular

weight of 100 000 to 2 500 000 g/mol. Typically, the molecular weight is in the range of 200 000 to 2 000 000 g/mol or 350 000 to 1 500 000 g/mol, or 600 000 to 1 300 000 g/mol, or 650 000 to 1 250 000 g/mol, or 700 5 000 to 1 200 000 g/mol, or 750 000 to 1 150 000 g/mol, or 800 000 to 1 100 000 g/mol calculated by PEO calibrated SEC.

The molecular weight of cationised alpha-glucan may be measured according to size-exclusion chromatography (SEC) using the Malvern Panalytical OMNISEC system. The eluent may be a 0.3125 M CH₃COOH + 0.3125 M CH₃COONa solution with a flow rate of 0.5 mL/min at 35°C. The column set may consist of three columns (a 15 TSKgel PWXL guard column and two TSKgel GMPWXL columns). A refractive index detector may be used for detection. Molecular weights and PDIs may be determined using conventional calibration with poly(ethylene oxide)/poly(ethylene glycol) narrow molecular weight distribution standards (Polymer Standards Service). Ethylene glycol (1mg/mL) may be used as a flow marker. Results may be calculated using the OmniSEC software from Malvern. Samples may be dissolved in ultrapure MilliQ-water by heating in 95-100°C for 30 minutes and 20 diluted with eluent including the flow marker. Measured values are extrapolated in the case they are outside the calibration standard line. 25

It has been found that these molecular weights contribute to the surprisingly good strength properties of the cationic alpha-1,3-glucan paper, board, or the like, strength agent. Further, the inventors have found that cationic alpha-1,3-glucan possessing these molecular weights do not start to floc, which can be an issue. 30

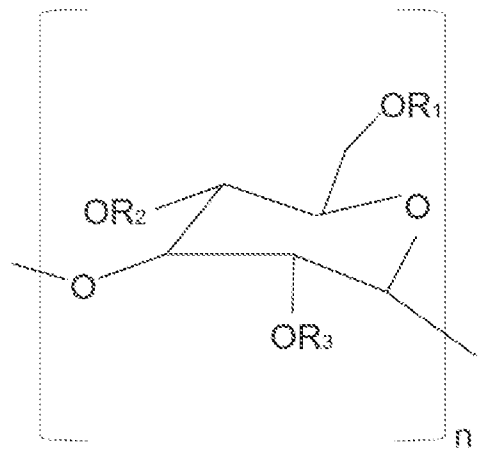
The paper, board, or the like, strength agent according to the first aspect of the invention may comprise at least 50 weight-% cationic alpha-1,3-glucan. Typically, the strength agent comprises at least 70 weight-%, or at least 80 weight-%, or at least 90 weight-%, or at least 95 weight-%, or at least 99 weight-% cationic alpha-1,3-glucan. The strength agent may contain up to 100 weight-% cationic alpha-1,3-glucan.

The cationic alpha-1,3-glucan of the paper, board, or the like, strength agent according to the first aspect of the invention may have an intrinsic viscosity (IV) of 1 to 5 dl/g, preferably 1.5 to 4.5 dl/g, or 2 to 4 dl/g, or 2.5 to 3.5 dl/g.

It has been found that the above IVs are useful because the IV correspond to the molecular weight of the polymer and the polymers according to the invention, having the above mentioned IV, causes less flocculation (as higher molecular weight polymers do). Further, polymers according to the invention cause less fixing of colloidal material (as lower molecular weight polymers do). The polymers according to the invention are capable of forming bonds between the fibres thus strengthening the fibre web.

The intrinsic viscosity may be measured in a known manner in 1 N NaCl at 25 °C by using an Ubbelohde capillary viscometer.

The cationic alpha-1,3-glucan of the paper, board, or the like, strength agent according to the first aspect of the invention may be represented by the structure,



wherein R_1 , R_2 and R_3 are independently H or a positively charged organic group, and wherein n is at least 200.

5

The " n " describes the amount of polymerized units. The term "degree of polymerization, DP, is typically used in polymer chemistry to describe the " n ".

10

According to the first aspect of the invention, n may be 200 to 7000. Typically, n may be in the range of 500 to 5000, or 1000 to 3000, or 2000 to 2500.

15

The degree of polymerization (DP) of uncationized alpha-1,3-glucan can be determined in the following way. An insoluble uncationized glucan polymer isolated from glucosyltransferase reactions may be treated with N,N-dimethylacetamide (DMAc) with 5% lithium chloride (LiCl) at 100 °C for 16 hours to form a glucan polymer solution. The solution (100 μ L) may then be injected into an Alliance™ 2695 HPLC (Waters Corporation, Milford, Mass.) equipped with a differential refractometer detector operating at 50 °C. The mobile phase may then be (DMAc containing 0.11 wt % LiCl) passed at a flow rate of 0.5 mL/min through four styrene-divinyl benzene columns in series; specifically, one KD-802, one KD-801, and two linear KD-806M columns (Shodex, Japan). The molecular weight of the glucan polymer sample may be

20

25

determined by comparison of retention time to a broad glucan standard. The Glucan DP may be obtained by dividing the molecular weight by 162.

5 The positively charged organic group of the paper, board, or the like, strength agent according to the first aspect of the invention may originate from a primary amine, secondary amine, tertiary amine, or a quaternary ammonium salt, preferably the positively
10 charged organic group is a trialkyl ammonium group, more preferably a trimethylammonium group, more preferably trimethylammonium hydroxypropyl.

R_1 may be the positively charged organic group
15 and R_2 and R_3 may be H.

 Without wishing to be bound by theory, it is believed that the positively charged organic group of the cationic alpha-1,3-glucan according to the invention
20 interacts with the carboxylic acid groups present in the cellulose of the paper, or board, or the like. It has been found that this interaction results in strong bonds between the strength agent and the cellulose, which result in the surprisingly good performance of the
25 strength agent.

 In one embodiment, the cationic alpha-1,3-glucan is linear.

30 The inventors have found that due to the cationic alpha-1,3-glucan being linear, surprisingly good strength properties are achieved.

 It is particularly useful to use a quaternary
35 ammonium group as the positively charged organic group because its charge does not depend on the pH.

The cationic alpha-1,3-glucan may be prepared according to conventional methods. For example, the patent applications no. WO 2016196022 and WO 2015095358 present methods for preparing cationic alpha-1,3-glucan.
5 can.

The cationic alpha-1,3-glucan according to the invention is particularly advantageous because it is biobased. Further, it has been found that the cationic
10 alpha-1,3-glucan according to the invention provides particularly good properties when used in applications with recycled fibres. The alpha-1,3-glucan is also surprisingly suitable to be added directly to the paper stock of paper, board, or the like, products. This is
15 advantageous since the production processes of the paper, board, or the like, products may be simplified.

Paper, board, or the like, product

20 According to a second aspect of the invention, a paper, board, or the like, product comprising the paper, board, or the like, strength agent according to the first aspect of the invention is provided.

25 The paper, board, or the like, product according to the second aspect of the invention may have a short span compression strength (SCT) index of 15 Nm/g to 30 Nm/g. The SCT index of the paper, board, or the like, product may be 20 Nm/g to 25 Nm/g, or 22 Nm/g to
30 24 Nm/g.

The paper, board, or the like, product according to the second aspect of the invention may have a burst index of 1.5 kPam²/g to 3.0 kPam²/g. The burst
35 index of the paper, board, or the like, product may be 1.8 kPam²/g to 2.5 kPam²/g, or 1.9 kPam²/g to 2.3 kPam²/g.

The paper, board, or the like, product according to the second aspect of the invention may have a crushing resistance (Corrugating Medium Test (CMT30)) index of 0.8 Nm/g to 1.3 Nm/g. The CMT30 index of the
5 paper, board, or the like, product may be 0.85 Nm²/g to 1.2 Nm²/g, or 0.9 Nm²/g to 1.1 Nm²/g.

The SCT index may be measured according to ISO 9895, the burst index according to ISO 2758 and the
10 CMT30 index according to ISO 7263.

Method for making paper, board, or the like

According to a third aspect of the invention,
15 a method for making a paper, board, or the like, product comprising,

- i) providing a fibre stock,
- ii) adding the paper, board, or the like, strength
20 agent according to the first aspect of the invention to the fibre stock,
- iii) forming a fibrous wet web,
- iv) optionally, wet pressing and/or drying the web, and
- 25 v) optionally, subjecting the web to size press treatment,

is provided.

30 The method may be performed in the above order.

The method may further comprise a step ia) between steps i) and ii) wherein the strength agent is solubilized in water. Typically, 1 weight-% to 10
35 weight-%, or 2 weight-% to 7 weight-%, or 2.5 weight-% to 4 weight-%, or 3 weight-% of the strength agent is solubilized in water.

The fibre stock of the method according to the third aspect of the invention may comprise recycled fibres and/or virgin fibres.

5

The recycled fibres and/or virgin fibres may have an ash content of 5 to 25 weight-%, or 10 to 20 weight-%. It has been found that the cationic alpha-1,3-glucan according to the invention may be used with
10 fibres having a higher ash content. The molecular weight and IV of the polymer gives better performance also with higher ash content fibres.

In one embodiment, the fibres originate from
15 mechanical or chemical pulp.

The pH of the fibre stock in step ii) of the method according to the third aspect of the invention is in one embodiment 4 to 9, or 5 to 8, or 6 to 7.5, or
20 6.5 to 7.5.

The paper, board, or the like, strength agent may be added in an amount of 0.5 kg/t to 5 kg/t, or 1 kg/t to 3 kg/t in relation to the fibre stock in the
25 method according to the third aspect of the invention.

It has been found that the aforementioned ratio of strength agent to the fibre stock has the added utility of providing sufficient strength to the paper while
30 still providing minimal stress on the environment. Further, the aforementioned ratio results in a negative z-potential. A positive z-potential can result in challenges during the paper making process.

35 Further, the water in methods for making paper, board, or the like, is usually circulated. There is thus a risk that the water turns cationic with time, when

using cationic strength agents. However, the inventors have found that the cationic alpha-1,3-glucan is effectively self-retaining, meaning that it will not be removed with the filtrate of the process and accumulate
5 in the water circulation system.

Examples

Reference will now be made in detail to various
10 embodiments.

The description below discloses some embodiments in such a detail that a person skilled in the art is able to utilize the embodiments based on the
15 disclosure. Not all steps or features of the embodiments are discussed in detail, as many of the steps or features will be obvious for the person skilled in the art based on this specification.

20 In the examples the presented DP value refers of non-ionic alpha-glucan measured by DP method as described on page 7. The molecular weight, Mw, of cationised alpha-glucan is measured by PEO calibrated by size exclusion chromatography method (SEC) as described on
25 page 5.

Example 1

In this study, the effect of linear cationic
30 alpha-1,3-glucan (AG) polymers on short span compression strength (SCT), burst strength and crushing resistance (Corrugating Medium Test (CMT30)) was tested. The performance of two cationized linear AGs with different degrees of substitution (DS 0.2 and N-bound 1,5%; DS
35 0.33 and N-bound 2,2%; both with a degree of polymerization (DP) of 1500 of uncationised alpha-glucan; intrinsic viscosity of 3 dl/g), were compared to on-site

produced glyoxylated polyacrylamide (Onsite GPAM, charge density 1.2 meq/g) and a typical cationic wet end starch (DS 0.035).

5 The tested furnish was prepared from recycled board (RCF) obtained from a German mill. 110 g/m² sheets were formed with a Rapid Koethen sheet former (RK) as follows: RCF was wet disintegrated in a 3% consistency at 70 °C with a Noviprofibre -pulper for 30sec at 500rpm
10 and 25min at 1000 rpm without soaking. The wet disintegrated pulp was further diluted to 1% with tap water and the pH and conductivity were adjusted to 6.8 and 3.0 mS/cm. Chemical additions were made to a mixing vessel (mixing speed 1000 rpm) and after chemical additions,
15 the pulp was poured to the RK sheet former and water was drained out through the wire with suction. Sheets were made in a recirculation mode: first six sheets were thrown away and after that 4 sheets were made for testing. The sheets were removed from the wire and vacuum
20 dried at 92 °C in restrain. Before testing in the laboratory, the sheets were pre-conditioned for 24 h at 23 °C in 50 % relative humidity, according to the standard ISO 187.

25 The table below shows the testing devices and standard methods used for the produced paper sheets.

Table 1. Sheet testing devices and standard methods used for the produced paper sheets.

Measurement	Device	Standard
Basis weight	Mettler Toledo	ISO 536
Short Span Compression test (SCT)	Lorentzen & Wettre	ISO 9895
Burst strength	Lorentzen & Wettre	ISO 2758
Corrugating Medium Test (CMT30)	Lorentzen & Wettre	ISO 7263

Table 2 shows the effect of different strength systems on board properties. The chemical amounts are given in kg dry chemical per ton dry RCF fibre stock.
5 All the test points include retention aids (Cationic polyacrylamide (CPAM) 400 g/t and Silica 400 g/t).

Table 2. Effect of different strength systems on board properties

Additive	SCT index [Nm/g]	Burst index [kPam ² /g]	CMT30 [Nm ² /g]
No strength additives	20.23	1.60	0.86
Onsite GPAM, 1.5kg/t	22.56	1.75	0.95
Onsite GPAM, 2.5kg/t	24.69	2.09	0.97
AG DS0.2, 1.5kg/t	23.35	1.85	0.96
AG DS0.2, 2.5kg/t	24.04	1.97	0.98
AG DS0.33, 1.5kg/t	22.87	1.82	0.98
AG DS0.33, 2.5kg/t	23.58	2.17	1.02
Starch DS 0.035, 2.5kg/t	21.52	1.71	0.89
Starch DS 0.035, 5kg/t	21.79	1.83	0.87

10

As seen in the table, the AGs improved significantly all the strength properties. The strength increase was comparable to on-site GPAM and significantly higher than with starch.

15

Example 2

In this study, Example 1 was repeated with three linear cationic alpha-1,3-glucan (AG) polymers (DS 0.2 ; DS 0.41 and N-bound = 2,6 %; DS 0.57 and N-bound = 3,2 %); intrinsic viscosity of 3 dl/g.

Table 3 shows the effect of the different AGs on board properties. The chemical amounts are given in kg dry chemical per ton dry RCF fibre stock. All the test points include retention aids (CPAM 400 g/t and Silica 400 g/t).

Table 3. Effect of different AGs on board properties

Additive	SCT index [Nm/g]	Burst index [kPam ² /g]	CMT30 [Nm ² /g]
No strength additives	19.85	1.83	0.85
AG DS0.2, 1.5kg/t	21.73	2.14	0.96
AG DS0.2, 2.5kg/t	23.41	2.39	1.02
AG DS0.41, 1.5kg/t	22.45	2.16	0.97
AG DS0.41, 2.5kg/t	23.93	2.32	1.03
AG DS0.57, 1.5kg/t	23.05	2.32	0.95
AG DS0.57, 2.5kg/t	22.50	2.32	0.95

As seen in the above table, all AGs with different charge densities significantly improved all the strength properties.

Example 3

In this study, Example 1 was repeated with two linear cationic alpha-1,3-glucan (AG) polymers with different degrees of polymerizations (DP 800 of uncationized glucan, Mw 450 000 g/mol of cationized glucan, intrinsic viscosity of 1,5 dl/g and DP 1500, Mw 840 000 g/mol, intrinsic viscosity of 3 dl/g) and the same DS (DS 0.2; DS 0.24 and N-bound = 1,7 %).

Table 4 shows the effect of different AGs on board properties. The chemical amounts are given in kg dry chemical per ton dry RCF fibre stock. All the test points include retention aids (CPAM 400 g/t and Silica 400 g/t).

Table 4. Effect of different AGs on board properties

Additive	SCT index [Nm/g]	Burst index [kPam ² /g]	CMT30 [Nm ² /g]
No strength additives	20.62	1.91	0.97
AG DP800, 1.5kg/t	22.18	2.12	1.01
AG DS800, 3kg/t	22.37	2.31	1.09
AG DP1500, 1.5kg/t	21.82	2.14	1.05
AG DP1500, 3kg/t	22.61	2.39	1.07

As seen in the above table, both AGs with different DPs significantly improved all the strength properties.

Example 4

The solubility of three different linear cationic alpha-1,3-glucan (AG) samples (DP 1500 of alpha-

1,3-glucan, Mw about 840 000 g/mol of cationized glucan, intrinsic viscosity of 3 dl/g) with different cationic substitution level were tested (DS 0.05, 0.2 and 0.4).

5 The solubility was determined as follows: 1 g of linear cationic alpha-1,3-glucan (as active) was dissolved in 150 ml of ionized water in a 250 ml beaker and mixed with a magnetic stirrer for 30 minutes. The temperature was 22 °C and pH 7. After dissolution the sample
10 was diluted with 80 ml of water and the sample was poured into a funnel and filtered through a pre-weighed filter fabric (100mm) with suction. The sample was washed two times with ionized water (70ml and 150 ml respectively). After the filtration, the filter fabric was removed and
15 dried in a drying oven (110 °C) for 4 hours. After drying, the filter was weighed and the amount of insolubles was calculated as follows:

$$insolubles(\%) = 100 * \frac{filter_{after}(g) - filter_{pre-weighed}(g)}{amount\ of\ sample(g)}$$

20

The results are seen in table 5.

Table 5. Solubility of AGs with different charge densities

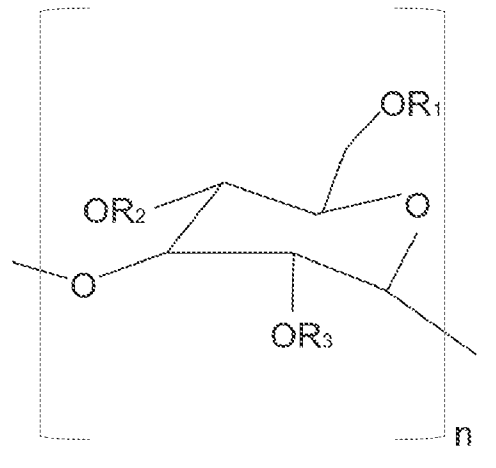
Sample	Insolubles, %
AG DS 0.05	26
AG DS 0.2	0
AG DS 0.4	0

25

Linear cationic alpha-1,3-glucan with higher charge density (DS 0.2 and DS 0.4) dissolved completely and no insolubles were detected (Table 1). The sample with the lowest charge density resulted in a significant
30 amount of insolubles.

CLAIMS

1. A paper, board, or the like, strength agent, comprising cationic alpha-1,3-glucan, wherein the cationic alpha-1,3-glucan is water soluble, wherein the cationic alpha-1,3-glucan is represented by the structure,



wherein R_1 , R_2 and R_3 are independently H or a positively charged organic group and wherein the cationic alpha-1,3-glucan has a molecular weight of 350 000 to 1 500 000 g/mol calculated by PEO calibrated SEC, and wherein the cationic alpha-1,3-glucan has a degree of cationic substitution of 0.15 to 0.5.

2. The paper, board, or the like, strength agent according to claim 1, wherein the cationic alpha-1,3-glucan has a degree of cationic substitution of 0.15 to 0.35, or 0.17 to 0.25.

3. The paper, board, or the like, strength agent according to claims 1 or 2, wherein the cationic alpha-1,3-glucan has a solubility of at least 90 wt.-% in water at a temperature of 22 °C, when 1 g was dissolved to 150 ml of water.

4. The paper, board, or the like, strength agent according to any one of the preceding

claims, wherein the cationic alpha-1,3-glucan has a molecular weight of 600 000 to 1 300 000 g/mol, calculated by PEO calibrated SEC.

5. The paper, board, or the like, strength agent according to any one of the preceding claims, wherein the cationic alpha-1,3-glucan has intrinsic viscosity (IV) 1 to 5 dl/g, preferably 1.5 to 4.5 dl/g.

6. The paper, board, or the like, strength agent according to any one of the preceding claims, wherein the paper, board, or the like, strength agent comprises at least 50 weight-%, or at least 70 weight-%, or at least 80 weight-%, or at least 95 weight-% cationic alpha-1,3-glucan.

7. The paper, board, or the like, strength agent according to any one of the preceding claims, wherein n is 200 to 7000, or 500 to 5000.

8. The paper, board, or the like, strength agent according to any one of the preceding claims, wherein the positively charged organic group originates from a primary amine, secondary amine, tertiary amine, or a quaternary ammonium salt, preferably the positively charged organic group is a trialkyl ammonium group, more preferably a trimethylammonium group, more preferably trimethylammonium hydroxypropyl.

9. A paper, board, or the like, product comprising the paper, board, or the like, strength agent according to claim 1.

10. The paper, board, or the like, product according to claim 9, wherein the paper, board, or the like, product has a SCT index of 15 Nm/g to 30 Nm/g

and/or a burst index of 1.5 kPam²/g to 3.0 kPam²/g and/or a CMT30 index of 0.8 Nm²/g to 1.3 Nm²/g.

11. A method for making a paper, board, or the like, product comprising,

- i) providing a fibre stock,
- ii) adding the paper, board, or the like, strength agent according to claim 1 to the fibre stock,
- iii) forming a fibrous wet web,
- iv) optionally, wet pressing and/or drying the web, and
- v) optionally, subjecting the web to size press treatment.

12. The method according to claim 11, wherein the fibre stock comprises recycled fibres and/or virgin fibres.

13. The method according to claims 11 or 12, wherein the pH of the fibre stock in step ii) is 4 to 9, or 6.5 to 7.5.

14. The method according to any of claims 11 to 13, wherein the paper, board, or the like, strength agent is added in an amount of 0.5 kg/t to 5 kg/t, or 1 kg/t to 3 kg/t in relation to the fibre stock.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2024/050289

A. CLASSIFICATION OF SUBJECT MATTER INV. D21H17/24 D21H21/18 D21H27/10 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) D21H Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2020/062929 A1 (BEHABTU NATNAEL [US]) 27 February 2020 (2020-02-27) paragraphs [0149], [0240]; claims 1-15 -----	1 - 14
A	WO 2016/196022 A1 (DU PONT [US]) 8 December 2016 (2016-12-08) claims 1-15; example 8 -----	1 - 14
A	WO 2019/004950 A1 (SCG PACKAGING PUBLIC COMPANY LTD [TH]) 3 January 2019 (2019-01-03) claims 1-26 -----	1 - 14
☐ 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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "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 5 July 2024		Date of mailing of the international search report 16/07/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Ponsaud, Philippe

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2024/050289

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2020062929 A1	27-02-2020	AU 2017362950 A1	02-05-2019
		BR 112019009836 A2	20-08-2019
		CN 109983067 A	05-07-2019
		EP 3541870 A1	25-09-2019
		JP 7125946 B2	25-08-2022
		JP 2019537678 A	26-12-2019
		US 2020062929 A1	27-02-2020
		WO 2018093748 A1	24-05-2018

WO 2016196022 A1	08-12-2016	AU 2016270307 A1	23-11-2017
		AU 2019216602 A1	29-08-2019
		BR 112017025808 A2	07-08-2018
		CA 2985685 A1	08-12-2016
		CN 108124456 A	05-06-2018
		DK 3540122 T3	09-11-2020
		EP 3303697 A1	11-04-2018
		EP 3540122 A1	18-09-2019
		ES 2827832 T3	24-05-2021
		HR P20191813 T1	27-12-2019
		HR P20201760 T1	19-03-2021
		JP 6956013 B2	27-10-2021
		JP 2018516316 A	21-06-2018
		KR 20180014741 A	09-02-2018
		SI 3303697 T1	28-02-2020
		US 2018119357 A1	03-05-2018
		US 2022136173 A1	05-05-2022
		WO 2016196022 A1	08-12-2016

WO 2019004950 A1	03-01-2019	PH 12019550296 A1	11-01-2021
		WO 2019004950 A1	03-01-2019
