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(54) Method for manufacturing paper, and paper manufactured thereby

(57) The invention relates to a method for manufacturing paper, which comprises adding to an aqueous suspension of cellulose fibers a water-soluble or dissolved cationic starch, optionally in addition to other additives, and then forming paper from this suspension in the conventional manner. The method according to the invention is characterized in that as cationic starch a cationic amylopectin potato starch is used. The invention also relates to paper so manufactured.

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Description

This invention relates to a method for manufacturing paper, which comprises adding a cationic amylopectin potato starch, optionally in addition to other additives, to an aqueous suspension of cellulose fibers and then forming paper from this suspension in the conventional manner.

By grinding raw materials used for paper-making, a fibrous pulp is obtained, in which the fibers are in a condition suitable for the paper formation. Various additives can be added to this fibrous pulp, such as resin glue, synthetic sizing agents, pigments and fillers (clay, titanium dioxide, talc, calcium carbonate, calcium sulphate), alum, retention agents and colloidal binders. The pulp mass is fed to a paper machine, where the paper formation takes place. The added additives serve *inter alia* to impart greater strength to the paper and to improve its writing and/or printing properties. Typically used as colloidal binder in paper-making is cationic starch.

The use of cationic starch in paper-making is described in U.S. Patent 2,935,436. According to this patent specification, the use of cationic starch provides a number of advantages over the use of non-cationic starch. Mentioned as advantages are: increased retention of starch, fillers and pigments; increased paper strength (bursting strength, breaking strength, folding strength and picking resistance) and lower dosage. As raw material for the manufacture of the cationic starch which according to U.S. Patent 2,935,436 is used in paper-making, different kinds of starch can be used, such as maize starch, wheat starch, potato starch, waxy maize starch, sago starch or rice starch.

Most kinds of starch consist of granules in which two types of glucose polymers occur, viz. amylose (15-35% by weight on dry substance) and amylopectin (65-85% by weight on dry substance). Amylose consists of non-branched or little branched molecules having an average degree of polymerization of 1,000 to 5,000 (depending on the kind of starch). Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of about 2,000,000. The commercially most important types of starch, viz. maize starch, potato starch, wheat starch and tapioca starch, contain 15-30% by weight of amylose.

Of some cereal types, viz. barley, maize, millet, milo, rice and sorghum, there exist natural varieties of which the starch granules consist substantially completely of amylopectin. Calculated as a percentage by weight of the dry substance, these starch granules contain more than 95% and usually more than 98% of amylopectin. The amylose content of these cereal starch granules is therefore less than 5% and usually less than 2%. It has been found that during the formation of amylopectin cereal starch granules in the grain plant, the enzyme that catalyzes the synthesis of amylose molecules is absent. The above cereal varieties are sometimes designated as waxy cereal grains and the amylopectin starch granules isolated therefrom as waxy cereal starches.

From EP-A-0,353,212 it is known to use cationic starch having an amylopectin content of at least 85% in paper-making. The required amylopectin content can be achieved by fractionating an amylose-containing starch. Preferably, however, a cereal variety is used that already has a very high amylopectin content by nature, such as waxy maize starch, which contains 99-100% amylopectin.

In contrast with the situation regarding various grains, there are no known natural potato varieties of which the starch granules consist substantially exclusively of amylopectin. The potato starch granules isolated from potato tubers typically contain approximately 20% amylose and 80% amylopectin (% by weight on dry substance). The past decade, however, saw the successful breeding, through genetic modification, of potato plants which, in the potato tubers, form starch granules that comprise more than 95% by weight (on the dry substance) of amylopectin.

In the formation of starch granules in the plant, various enzymes are catalytically active. Of these enzymes, the granule-bound starch synthase (GBSS) is involved in the formation of amylose. The synthesis of the GBSS enzyme is dependent on the activity of genes that code for the GBSS enzyme. Elimination or inhibition of the expression of these specific genes leads to the synthesis of the GBSS enzyme being prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material. An example of this is the amylose-free mutant of the potato (amf) the starch of which contains substantially exclusively amylopectin as a result of a recessive mutation in the GBSS gene. This mutation technique is described *inter alia* in the following two journal articles:

- J.H.M. Hovenkamp-Hermelink et al.
  Isolation of amylose-free starch mutant of the potato (Solanum tuberosum L.)
  Theor. Appl. Genet. (1987), 75: 217-221.

- E. Jacobsen et al.
  Introduction of an amylose-free (amf) mutant into breeding of cultivated potato, Solanum tuberosum L.
  Euphytica (1991), 53, 247-253.

Elimination or inhibition of the expression of the GBSS gene in the potato is also possible by the use of so-called antisense inhibition. This genetic modification of the potato is described in the Canadian patent specification 2,061,443; the International patent specification WO 92/11376 and in the following journal article:

- R.G.F. Visser et al.
  Inhibition of the expression of the gene for granule-bound starch synthase in potato by antisense constructs.
  Mol. Gen. Genet. (1991), 225: 289-296.

By the use of genetic modification it has been found to be possible to breed and grow potatoes whose starch granules contain little or substantially no amylose.

The term amylopectin potato starch is herein understood to mean the potato starch granules, isolated from potato tubers, having an amylopectin content of at least 95% by weight, calculated on the dry substance.

With regard to production possibilities and properties, there are significant differences between amylopectin potato starch on the one hand and the waxy cereal starches on the other. This also holds, in particular, for waxy maize starch, which is commercially by far the most important waxy cereal starch. The cultivation of waxy maize, which is suitable for the production of waxy maize starch, is commercially unfeasible in countries with a cold or temperate climate, such as the Netherlands, Belgium, England, Germany, Poland, Sweden and Denmark. For the growth of potatoes, on the other hand, the climate in these countries is quite suitable.

The composition and properties of amylopectin potato starch differ from those of the waxy cereal starches. For instance, amylopectin potato starch has a much lower content of lipids and proteins than the waxy cereal starches. Problems regarding odour and foam formation, which may arise on account of the lipids and proteins when using waxy cereal starch products (native and modified), do not arise or do so to a much lesser extent when corresponding amylopectin potato starch products are used. Unlike the waxy cereal starches, amylopectin potato starch contains chemically bound phosphate groups. As a result, in dissolved condition amylopectin potato starch products have a specific polyelectrolyte character.

It has been found that cationic amylopectin potato starch is eminently suitable for use as colloidal binder in paper-making. With regard to drainage, retention and paper strength, cationic amylopectin potato starch gives equivalent or better results compared with corresponding cationic derivatives of other starch raw materials.

The invention accordingly relates to a method for the manufacture of paper, which comprises adding to an aqueous suspension of cellulose fibers a water-soluble or dissolved cationic amylopectin potato starch, optionally in addition to other additives, and then forming paper from this suspension in conventional manner.

Methods for manufacturing cationic starch have been described by D.B. Solarek: Cationic Starches, in the book of O.B. Wurzburg (Ed.): Modified Starches: Properties and Uses, CRC Press Inc., Boca Raton, Florida, 1986, pp. 113-130. The methods described therein can also be used for the preparation of cationic amylopectin potato starch. According to the invention, it is preferred to use cationic amylopectin potato starch products that contain electropositively charged quaternary ammonium groups. Before, after or during the cationization reaction the amylopectin potato starch may be additionally modified physically, chemically and/or enzymatically. The invention also embraces the use of these additionally modified amylopectin potato starch products. The degree of substitution (DS) of the cationic amylopectin potato starch to be used according to the invention is preferably between 0.005 and 0.5 and more preferably between 0.01 and 0.2.

The amount of cationic amylopectin potato starch which according to the invention is included in the paper pulp depends inter alia on the kind of pulp used, the working conditions used and the desired paper properties. Preferably, 0.05 to 10% by weight and more preferably 0.1 to 2% by weight of starch derivative (dry substance) calculated on the paper pulp (dry substance) is used.

The cationic amylopectin potato starch to be used according to the invention is preferably first gelatinized in water, whereafter the resultant starch solution (optionally after dilution) is added to the pulp mass. It is also possible, however, to mix pre-gelatinized cold-soluble cationic amylopectin potato starch (as dry product or after dissolution in water) with the pulp mass.

The cationic amylopectin potato starch can be added at any point in the paper-making process. The cationic starch product can therefore be added to the pulp while it is disposed in the head box, the Hollander, the hydropulper or the dusting box. If desired, in addition to the cationic amylopectin potato starch, an anionic amylopectin potato starch can also be added to the pulp. (SW 50).

<u>Example 1</u>

In this example the following four cationic starch products, containing quaternary ammonium substituents (Degree of Substitution 0.035), were used as wet-end additive for the manufacture of paper:

A. Cationic maize starch
B. Cationic potato starch
(containing about 20% by weight of amylose on dry substance)
C. Cationic waxy maize starch

D. Cationic amylopectin potato starch
(according to the invention).

The cationic starch products were slurried in water, forming a starch suspension with 10% by weight of starch. This suspension was gelatinized with steam. The obtained starch solution was diluted with water to 1% by weight dry substance.

The test pulp was prepared by mixing a diluted fiber suspension (containing 100% bleached birch sulphate on dry substance), with 20% by weight (calculated on dry cellulose fiber) of calcium carbonate (filler) and diluted starch solution. The amount of added cationic starch was 1.25% by weight (dry substance) calculated on the dry fiber. The consistency of the tested pulp was 0.4%. The test pulps were made into handsheets with a FRET sheetformer. The handsheets were dried in vacuum dryers to a moisture content of 7% by weight.

The properties of the formed paper were determined with the following test methods:

Paper test	Apparatus/materials	Test method
Sheet weight	Balance	NEN 1109
Bursting strength	Lorentzen & Wettre type 14-1 Burstomatic	NEN 1765 Tappi T403 -om-85
Tensile strength	Adamel Lhomargy type DY-20	NEN 1249 Tappi T494 -om-88
Internal Bond	Schröder-Werkstoff Prüfmaschinen type SN.22.91.1007	Tappi T506 -wd-83 UM 584
Starch content	Spectrophotometer	Hexokinase method according to Boehringer

The test results are recorded in Table 1.

TABLE 1

Cationic starch	Starch content (%)	Ash content (%)	Sheet weight (g/m²)	Bursting strength (kPa)	Tensile strength (kN/m)	Internal Bond (J/m²)
Maize starch	1.0	16.9	98.7	271	7.3	740
Potato starch	0.9	15.1	98.9	305	6.9	760
Waxy maize starch	1.0	16.4	98.6	306	6.8	820
Amylopectin potato starch	1.0	16.4	97.7	310	7.2	830
Control	< 0.1	5.9	85.8	210	6.3	645

As will be noted from the foregoing results, the cationic amylopectin starch gave equivalent or higher strength values in the paper test sheets, as compared to the other cationic starch products.

Example 2

In this example various amounts of cationic amylopectin potato starch products (containing quaternary ammonium substituents with a DS of 0.035) were used as wet-end additive for papermaking. This series of tests was carried out in a pilot paper machine located at the Hercules European Research Center in Barneveld.

The pulp used comprised an aqueous slurry of 70% by weight (on dry substance) of short fiber and 30% by weight of long fiber. Calcium carbonate (20% by weight on dry pulp) was added to the stock. The pulp was beaten with a consistency of 1.8% in a Pilao refiner to 27°SR. The pulp was diluted with water containing 100 ppm $CaCl_2$ and 150 ppm $NaHCO_3$.

The cationic amylopectin potato starch was slurried in water (10% dry substance) and cooked with steam (25 minutes; 850 rpm). The starch solution was added in quantities of 0.75%, 0.875% and 1.0% by weight of dry starch calculated on dry fiber. The pulp was further diluted with white water.

The pulp was made into paper in the pilot paper machine at a speed of 3.0 m/min. After the pressing section of the machine the sheet had a dry substance content of about 40%. The sheet was dried on drying cylinders to a moisture content of 4%. The paper was tested and the results of these tests are recorded in Table 2. These results show the higher strength values in the paper prepared with increasing amounts of cationic amylopectin potato starch.

TABLE 2

Cationic amylopectin potato starch; % by wt. of dry product on dry fiber	Starch content (%)	Ash content (%)	Sheet weight (g/m²)	Bursting strength (kPa)	Tensile strength (kN/m)	Internal Bond (J/m²)
0.75	0.704	16.64	78.96	217.2	5.338	5.272
0.875	0.757	16.64	78.59	229.7	5.498	5.274
1.00	0.836	16.04	80.05	234.9	5.632	5.315

Example 3

In this example the following cationic starches, all containing quaternary ammonium substituents with a degree of substitution of 0.035, were tested as a wet-end additive for the production of paper:

A. Cationic potato starch (containing approximately 20% by weight amylose on dry substance)
B. Cationic waxy maize starch
C. Cationic amylopectin potato starch
(according to the invention).

A slurry of each of the cationic starches, with 10% by weight starch, was gelatinized with steam. The obtained starch solution was diluted with water to 1% by weight dry substance. The pulp consisted of 80% by weight bleached birch sulphate and 20% by weight calcium carbonate as a filler (both calculated on consistency). The pulp had a consistency of 0.6%. The sheets were made with a FRET sheetformer, obtained from the CTP in Grenoble. The amount of starch added to the pulp was 0.55% and 0.65% by weight, calculated as dry substance on consistency. Before dewatering, the pulp with the added starch was diluted to 0.3%. The handsheets were dried in vacuum dryers to a moisture content of approximately 4% by weight.

The obtained paper was tested according to the above-mentioned test methods, after being conditioned to a temperature of 23°C and a relative humidity of 50%. The results of the tests are collected in the following Tables 3 (0.55% added starch) and 4 (0.65% added starch).

TABLE 3

Cationic starch	Starch dosage (%)	Sheet weight (g/m²)	Filler content (%)	Bursting strength (kPa)	Tensile strength (kN/m)	Internal Bond (J/m²)
Potato starch	0.55	75.08	9.99	182.4	3.40	466.0
Waxy maize starch	0.55	74.79	9.34	178.1	3.446	480.1
Amylopectin potato starch	0.55	75.13	10.18	182.2	3.503	495.5

TABLE 4

Cationic starch	Starch dosage (%)	Sheet weight (g/m^2)	Filler content (%)	Bursting strength (kPa)	Tensile strength (kN/m)	Internal Bond (J/m^2)
Potato starch	0.65	75.82	9.40	189	3.619	477
Waxy maize starch	0.65	75.52	9.10	180	3.678	494
Amylopectin potato starch	0.65	75.74	9.66	206	3.697	512

It is clear that the addition of cationic amylopectin potato starch results in higher filler retentions than the addition of one of the other cationic starches. With other things being equal, a higher filler content will cause a decrease of the strength of the paper. However, the results show that with cationic amylopectin potato starch the strength properties of the paper sheets are equivalent, and with regard to the internal strength even higher, than obtained with the other cationic starches. It can be concluded that with cationic amylopectin potato starch higher filler retentions and equivalent or higher strength values of the paper are obtained than with other cationic starches.

Claims

1. A method for manufacturing paper, which comprises adding to an aqueous suspension of cellulose fibers a water-soluble or dissolved cationic starch, optionally in addition to other additives, and then forming paper from this suspension in the conventional manner, characterized in that as cationic starch a cationic amylopectin potato starch is used.

2. A method according to claim 1, characterized in that the amylopectin potato starch is isolated from potatoes originating from potato plants obtained by mutation.

3. A method according to claim 1, characterized in that the amylopectin potato starch is isolated from potatoes originating from potato plants obtained by antisense inhibition.

4. Paper manufactured utilizing the method according to claims 1-3.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2472

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO-A-86 00100 (EKA AB) * page 10, line 30 - page 11, line 15; claims 1,4 *	1,4	D21H17/24 D21H17/29
D,A	EP-A-0 353 212 (GRACE) * claims 1-7 *	1-4	
A	EP-A-0 139 597 (ROQUETTE FRERES) * claims 1-8 *	1-4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 December 1995	Fouquier, J-P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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