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(54) Process for making paper using cationic amylopectin starch

(57) The invention relates to the field of papermaking. More in particular, the invention relates to a method of reducing the phenomenon of vessel picking in papermaking. In accordance with the invention it has surprisingly been found that the problem vessel picking may be significantly reduced by using a cationic amylopectin starch in the paper pulp, i.e. in the wet-end.

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Description

[0001] The invention relates to the field of papermaking. More in particular, the invention relates to improvements in papermaking from hardwood pulps, such as eucalyptus.

[0002] Over the past years, eucalyptus pulps have risen to prominence in papermaking by virtue of their rapid rates of their tree growth and their benefits to sheet uniformity and printability. This extends not only to printing and writing grades of paper, but also to white top linerboard. Eucalyptus, such as *E. grandis* and *E. globulus,* are generally associated with the Iberian Peninsula and Latin America. In other regions of the world, there are sound logistical reasons for using indigenous species as alder, acacia, birch and oak.

[0003] All hardwoords have some common structural features in the wood, most notably the vessels, which ramify through the stem and act as water pipes, distributing water from the roots to other parts of the tree. Vessels are normally much wider than the fibers, which is responsible for many of the problems caused by vessels in papermaking. The inclusion of the hardwood vessels in the furnish has caused some serious print quality problems in many hardwoord pulps, especially with eucalyptus.

[0004] When these pulps were first introduced into the market, uncoated papers that used them in the furnish suffered from picking of vessels from the surface of the sheet. The picking not only damaged the paper surface, it accumulated on the press blankets, requiring stoppage for wash-ups in the middle of a run and lost time to the printer. There was also a danger of the vessels causing pull-outs on coated grades by locally weakening the adhesion of the coating to the paper surface.

[0005] Over time, papermakers have made various attempts to contain the problem, often by improved surface sizing, and claims from printers for vessel picking could sometimes be reduced to tolerable levels. However, the improved surface sizing partially negated the cost advantage of hardwood pulps.

[0006] Furthermore, in the last four to five years the problem has reemerged and in worsened form as offset press speeds have increased with a new generation of presses that print five or six colors. Apart from vessel picking, the incidence of ink refusal in uncoated papers has come to the fore. Ink refusal is manifested as white spots where the vessel is still clearly present when the printed paper is examined under the microscope. Picking implies poor bonding of the vessels to the other fibers and fines, but ink refusal in an offset litho press implies low surface energy (poor wetting) and/or a local variation in compressibility that reduces ink transfer.

[0007] In accordance with the invention it has surprisingly been found that the problem vessel picking may be significantly reduced by using a specific starch in the paper pulp, i.e. in the wet-end. As a result, the previously necessary, more expensive, and elaborate surface sizing adaptations are obsolete. Under certain circumstances, surface sizing may be omitted completely, or can be substituted by a pre-coat operation.

[0008] Also, a consequence of the invention is that larger quantities of hardwood, such as eucalyptus, may be used in the pulp without encountering any strength or vessel picking problems, which may considerably reduce the cost of the paper produced without affecting the quality.

[0009] These and other advantages of the invention are attained, as mentioned by using a specific starch in the wet-end. The specific starch used according to the invention is an cationic amylopectin starch.

[0010] The use of cationic starch in papermaking has been described previously. For instance, US patent 2,935,436 discloses that a number of advantages is associated with the use of cationic starch instead of non-cationic starch. Examples of these advantages are increased retention of starch, fillers and pigments, increased paper strength (bursting strength, breaking strength, folding strength) and lower dosage. Further, European patent application 0 703 314 discloses a method for manufacturing paper wherein a cationic amylopectin potato starch is added to an aqueous solution of cellulose fibers, optionally in addition to other additives, followed by forming paper from this suspension in a conventional manner. It is described that a higher amount of fillers can be incorporated into the paper by making use of cationic amylopectin potato starch without a negative impact on paper strength, when compared to the use of cationic potato starch having a normal amylopectin content or waxy maize starch.

[0011] Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt.% on dry substance) and amylopectin (65-85 wt.% on dry substance). Amylose consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type. Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1,000,000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt.% amylose.

[0012] Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin. Calculated as weight percent on dry substance, these starch granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are also referred to as waxy cereal grains, and the amylopectin-starch granules isolated therefrom as waxy cereal starches.

[0013] In contrast to the situation of different cereals, root and tuber varieties of which the starch granules nearly exclusively consist of amylopectin are not known in nature. For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt.% on dry substance). During the past 15 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt.% (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

[0014] In the formation of starch granules, different enzymes are catalytically active. Of these enzymes, the granule-bound starch synthase (GBSS) is involved in the formation of amylose. The presence of the GBSS enzyme depends on the activity of genes encoding for said GBSS enzyme. Elimination or inhibition of the expression of these specific genes results in the production of the GBSS enzyme being prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material or by recessive mutation. An example thereof is the amylose-free mutant of the potato (amf) of which the starch substantially only contains amylopectin through a recessive mutation in the GBSS gene. This mutation technique is described in, inter alia, J.H.M. Hovenkamp-Hermelink et al., "Isolation of amylose-free starch mutant of the potato (Solanum tuberosum L.)", Theor. Appl. Gent., (1987), 75:217-221, and E. Jacobsen et al., "Introduction of an amylose-free (amf) mutant into breeding of cultivated potato, Solanum tuberosum L., Euphytica, (1991), 53:247-253.

[0015] Elimination or inhibition of the expression of the GBSS gene in the potato is also possible by using so-called antisense inhibition. This genetic modification of the potato is described in 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.

[0016] By using genetic modification, it has been found possible to cultivate and breed roots and tubers, for instance potato, yam, or cassave (Patent South Africa 97/4383), of which the starch granules contain little or no amylose. As referred to herein, amylopectin-potato starch is the potato starch granules isolated from potato tubers and having an amylopectin content of at least 95 wt.% based on dry substance.

[0017] Regarding production possibilities and properties, there are significant differences between amylopectin-potato starch on the one hand, and the waxy cereal starches on the other hand. This particularly applies to waxy maize starch, which is commercially by far the most important waxy cereal starch. The cultivation of waxy maize, suitable for the production of waxy maize starch is not commercially feasible in countries having a cold or temperate climate, such as The Netherlands, Belgium, England, Germany, Poland, Sweden and Denmark. The climate in these countries, however, is suitable for the cultivation of potatoes. Tapioca starch, obtained from cassava, may be produced in countries having a warm climate, such as is found in regions of South East Asia and South America.

[0018] The composition and properties of root and tuber starch, such as amylopectin-potato starch and amylopectin-tapioca starch, differ from those of the waxy cereal starches. Amylopectin-potato starch has a much lower content of lipids and proteins than the waxy cereal starches. Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using waxy cereal starch products (native and modified), do not occur, or occur to a much lesser degree when using corresponding amylopectin-potato starch products. In contrast to the waxy cereal starches, amylopectin-potato starch contains chemically bound phosphate groups. As a result, amylopectin-potato starch products in a dissolved state have a distinct polyelectrolyte character.

[0019] The invention contemplates the use of cationic starch obtained from cereal and fruit sources on the one hand, and root and tuber sources on the other hand. Of the cereal starches, waxy maize starch has proven very suitable. In general, however, root and tuber starches are more preferred. As has been indicated above, it is often advantageous to use a starch having a very low content of lipids and/or proteins. The use of cationic amylopectin-potato starch and amylopectin-tapioca starch as a strengthening agent in paper has been found to lead to a particularly strong paper sheet.

[0020] In accordance with the invention, an amylopectin starch is defined as a starch obtained from, or in the form of, starch granules comprising more than 95 wt.%, preferably more than 98 wt.%, based on dry substance, of amylopectin, which starch granules are isolated from a plant source, such as potato tubers or cassava roots, in which said starch granules are formed having the mentioned amylopectin content.

[0021] Methods of making cationic starch are known per se, and have for instance been elucidated by D.B. Solarek: Cationic Starches, in the book of O.B. Würzburg (Ed.): Modified Starches: Properties and Uses, CRC Press Inc., Boca Raton, Florida, 1986, pp. 113-130. The methods described in this book can also be used for the preparation of cationic amylopectin starch by using an amylopectin starch, of a particular chosen botanical source, as raw material.

[0022] According to the invention, it is preferred to use a cationic amylopectin starch that contains electropositively charged quaternary ammonium groups. Before, after or during the cationization reaction the amylopectin starch may be additionally modified physically, chemically and/or enzymatically. The invention also encompasses the use of these additionally modified amylopectin starches. The degree of substitution (DS) of the cationic amylopectin 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. Even though a wide variety of ammonium compounds, preferably quaternary ones, can be employed in the preparation of a cationic amylopectin starch for use in accordance with the present invention, it is preferred to prepare a cationic amylopectin starch by treating the amylopectin starch with 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride or 2,3-epoxypropyl-trimethyl ammonium chloride.

[0023] The amount of cationic starch that is used will depend on the kind of pulp that is used, the working conditions and the desired paper properties. Preferably, 0.05 to 10 wt.% and more preferably 0.1 to 2 wt.% of cationic amylopectin starch, dry substance, calculated on the paper pulp, dry substance, is used.

[0024] The cationic amylopectin starch is preferably first gelatinized in water. The resultant starch solution, optionally after further dilution, is added to the pulp mass. It is also possible, however, to mix pre-gelatinized cold-soluble cationic amylopectin starch with the pulp mass, either as dry product or after dissolution in water).

[0025] The cationic amylopectin starch can be added at any point in the papermaking process. For example, it can 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 starch, an anionic starch can also be added to the pulp.

[0026] As mentioned above, the invention specifically addresses problems associated with the use of pulps prepared from hardwood. Accordingly, it is preferred according to the invention that a pulp is used for papermaking which comprises at least 5 wt.%, based on dry substance, of hardwood pulp. More preferably, the pulp comprises at least 10 wt.%, based on dry substance, of hardwood pulp. Suitable sources of hardwood are oak, elm, eucalyptus, aspan, balsam cottonwood and acacia. In a preferred embodiment, the hardwood pulp is from eucalyptus. The remainder of the pulp, if the pulp is not entirely from hardwood, may be from various softwood sources, such as spruce, pine and larch.

[0027] It is one of the advantages of the invention, that surface treatments of the manufactured paper may be carried out to a lesser extent, or can be omitted altogether. Surface treatment of a paper sheet, such as surface sizing or coating, have conventionally be used to increase the vessel picking resistance of the paper to be manufactured. Typically, such surface treatments involve the use of starch.

[0028] Normal dosage levels of surface treatment starch are 5 to 10 wt.% based on the sheet weight. For a final sheet weight of 100 g/m^2 this means a starch pick-up of 2.5 to 5 g starch on each side of the paper sheet. Using a cationic amylopectin starch in the wet-end of the papermaking in accordance with the present invention, the starch pick-up in a surface treatment can be reduced by 10 to 40 %, due to the improved vessel picking resistance of the paper. Thus, the starch pick-up in a surface treatment in a process for manufacturing paper in accordance with the invention may be as low as from 0.5 to 6 wt.% based on the sheet weight, and preferably from 1 to 4 wt.% based on the sheet weight.

[0029] A reduction in starch pick-up will lead to a reduction in final sheet weight. This loss in sheet weight can be compensated by the addition of a pigment in the surface treatment formulation. Advantageously, by substituting surface treatment starch for pigment an overall reduction in cost prize is achieved.

[0030] The invention will now be elucidated by the following, non-restrictive examples.

Example 1

[0031] In this example the following two 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 potato starch (containing about 20 % by weight of amylose on dry substance, Amylofax PW)
B. Cationic amylopectin potato starch (according to the invention, containing about 2 % by weight of amylase on dry substance, PR0602A)

[0032] 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.

[0033] The test pulp consisted of a mixture of 38 % long fibers, 28 % short fiber (Eucalyptus) and 34 % CTMP. Calcium carbonate was added as filler to obtain a final ash content of 16 % in the paper sheet. The amount of added cationic starch was 1.0 % by weight (dry substance). The test pulp was made into hand sheets (sheet weight 80 g/m^2) with a hand sheet former. The hand sheets were dried to a moisture content of 7 % by weight.

[0034] The vessel picking tendency was determined by performing the linting with a Prufbau dry pick test as described in Tappi Journal, July 1994, page 185. The test ink was a high tack inkt (Huber 408004). The vessel picking tendency was assessed visually. The results are depicted in figure 1.

Example 2

[0035] In this example the same two cationic starch products, containing quaternary ammonium substituents (Degree of Substitution 0.035), were used as described in example 1.

[0036] The test pulp consisted of a mixture of 42 % long fibers, 8 % short fiber (Eucalyptus) and 50 % CTMP. Calcium carbonate was added as filler to obtain a final ash content of 16 % in the paper sheet. The amount of added cationic starch was 1.0 % by weight (dry substance). The test pulp was made into hand sheets (sheet weight 80 g/m^2) with a hand sheet former. The hand sheets were dried to a moisture content of 7 % by weight.

[0037] The vessel picking tendency was determined by performing the linting with a Prufbau dry pick test as described in Tappi Journal, July 1994, page 185. The test ink was a high tack inkt (Huber 408004). The vessel picking tendency was assessed visually. The results are depicted in figure 1.

Conclusion

[0038] For both pulp qualities (i.e. both Example 1 and 2), a remarkable improvement is observed in vessel picking tendency when cationic amylopectin potato starch is used compared to regular cationic potato starch

Claims

1. A process for making paper, wherein a cationic amylopectin starch is added to an aqueous suspension of cellulose fibers, and forming paper from this suspension in conventional manner, wherein the suspension of cellulose fibers comprises at least 5 wt. %, based on dry substance, of hardwood cellulose fibers.

2. A process according to claim 1, wherein the cationic amylopectin starch comprises at least 95 wt.%, preferably at least 98 wt.%, based on dry substance, of amylopectin.

3. A process according to any of the preceding claims, wherein the cationic amylopectin starch is a waxy maize starch or an amylopectin root or tuber starch.

4. A process according to claim 3, wherein the starch is a potato or tapioca starch.

5. A process according to any of the preceding claims, wherein the suspension of cellulose fibers comprises at least 10 wt.%, based on dry substance, of hardwood cellulose fibers.

6. A process according to any of the preceding claims, wherein the hardwood cellulose fibers are obtained from oak, elm, eucalyptus, aspan, balsam cottonwood, or acacia.

7. Paper obtainable by a process according to any of the preceding claims.

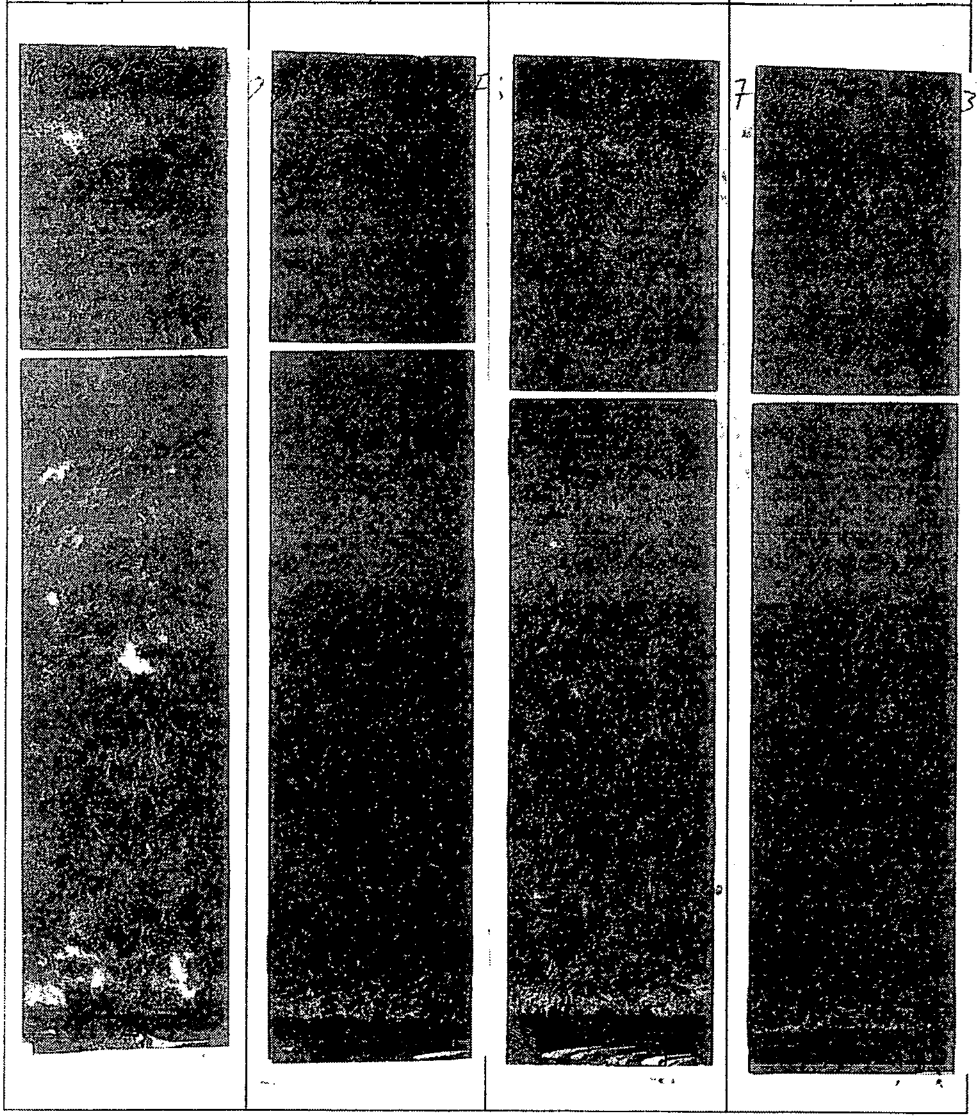
8. Use of a cationic amylopectin starch in the wet-end of papermaking from a pulp comprising at least 5 wt. % of hardwood pulp for reducing vessel picking.

Figure 1

Prüfbau linting test

Testink: Huber 408004 (very high tack)
Tested side : coded side
Speed: 0.5 m/sec.

LF 38 % KF 28 % CTMP 34 % Amylofax PW 1% Example 1	LF 38 % KF 28 % CTMP 34 % PR 0602 A 1% Example 1	LF 42 % KF 8 % CTMP 50 % Amylofax PW 1% Example 2	LF 42 % KF 8 % CTMP 50 % PR 0602 A 1% Example 2



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EUROPEAN SEARCH REPORT

Application Number
EP 06 07 6199

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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X	US 5 635 028 A (VINSON KENNETH D [US] ET AL) 3 June 1997 (1997-06-03) * column 4, line 26 - line 41 * * column 5, line 10 - line 42 * * column 9, line 18, paragraph 10 - column 10, line 40 * * column 18, line 56 - column 20, line 16 * -----	1-8	
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TECHNICAL FIELDS SEARCHED (IPC)

D21H

The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
The Hague	4 April 2007	Westberg, Erika

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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