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(54) **Method for surface sizing paper**

Verfahren zur Oberflächenleimung vom Papier

Procédé de collage en surface du papier

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Description

[0001] This invention relates to a method for surface sizing paper, in which use is made of degraded amylopectin potato starch products.

[0002] Paper and paperboard are often surface sized with sizing agents to improve the physical properties of paper and paperboard. The size binds the cellulose fibers of paper to each other and to the paper sheet, whereby the tensile strength and the bursting strength of the paper are increased. As a result, it is for instance possible to use an eraser without the fiber structure of the paper being destroyed. Surface sizing gives the paper a relatively smooth, hard surface layer, which counteracts the extraction of cellulose fibers when the paper is being written on with pen and ink. This surface layer further prevents the tip of the pen, biro or pencil from becoming hooked in the paper when the paper is being written on. Moreover, surface sizing reduces the porosity of the paper, since the surface pores of the paper are sealed. Thus the resistance to water and oil as well as the printability are increased. Surface sizing is important *inter alia* for writing paper, paper to be printed and certain kinds of packaging paper.

[0003] In industrial practice, many kinds of degraded starch products are used as surface sizing agent for paper. The term degraded starch products is herein understood to mean those starch products which, as a result of partial depolymerisation of the starch molecules (by means of acids, oxidants and/or enzymes), possess a reduced average molecular weight and a reduced viscosity in water. Degraded native starches, degraded starch esters and degraded starch ethers are used. Useful types of starch include potato starch, maize starch, wheat starch, tapioca starch, and waxy maize starch. The state of the art regarding the use of degraded starch products for surface sizing paper is described *inter alia* in the following two articles:

- W. Lüttgen Oberflächenstärke Wochenblatt für Papierfabrikation 1991, NO. 5, pp. 157-160

- R.F. Sirois The Latest Generation of Surface Sizing Starches Paper Technology, November 1992, pp. 31-33.

[0004] Most types of starch consist of granules in which two types of glucose polymers occur, viz. amylose (from 15 to 35% by weight, based on dry substance) and amylopectin (from 65 to 85% by weight, based on dry substance). Amylose consists of unbranched or little branched molecules of an average degree of polymerisation of from 1000 to 5000 (depending on the type of starch). Amylopectin consists of very large, highly branched molecules of an average degree of polymerisation of about 2,000,000. The commercially most important types of starch, viz. maize starch, potato starch, wheat starch and tapioca starch, contain from 15 to 30% by weight of amylose.

[0005] Of some types of cereal, viz. barley, maize, millet, milo, rice and sorghum, there exist natural varieties the starch granules of which consist substantially entirely of amylopectin. Calculated as a weight percentage based on 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 cereal plant, the enzyme that catalyzes the synthesis of amylose molecules is absent. The above cereal varieties are sometimes referred to as waxy cereal grains and the amylopectin starch granules isolated therefrom as waxy cereal starches.

[0006] In contrast with the situation regarding various grains, no potato varieties are known from nature of which the starch granules consist substantially exclusively of amylopectin. The potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (weight percentage based on dry substance). The past decade, however, saw the successful breeding, through genetic modification, of potato plants which form starch granules in the potato tubers which comprise more than 95% by weight (based on dry substance) of amylopectin.

[0007] 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, due to a recessive mutation in the GBSS gene. This mutation technique has been 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.

[0008] Elimination or inhibition of the expression of the GBBS gene in the potato is also possible by the use of so-

called antisense inhibition. This genetic modification of the potato has been described in Canadian patent specification 2,061,443; International patent specification WO 92/11376 and 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.

[0009] By the application of genetic modification it has been found possible to breed and grow potatoes the starch granules of which contain little or substantially no amylose. The term amylopectin potato starch is herein understood to mean the potato starch granules obtained from potato tubers obtained from genetically modified potato plants which form said granules in the potato tubers, said starch granules comprising more than 95% by weight, based on dry substance, of amylopectin.

[0010] As regards 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 growth of waxy maize, which is suitable for the production of waxy maize starch, is not commercially feasible in countries with a cold or temperate climate, such as the Netherlands, Belgium, England, Germany, Poland, Sweden, and Denmark. However, the climate in the above countries is suitable for the growth of potatoes.

[0011] 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 do. Problems regarding odor and foam formation, which may arise because of the lipids and/or proteins when using waxy cereal starch products (native and modified), do not occur, or do so to a much lesser extent, when use is made of corresponding amylopectin potato starch products. As opposed to the waxy cereal starches, amylopectin potato starch contains chemically bound phosphate groups. As a result, in dissolved condition amylopectin potato starch products possess a specific polyelectrolyte character.

[0012] It has been found that degraded amylopectin potato starch granules isolated from certain potato tubers are eminently suitable as a surface sizing agent for paper. Regarding strength improvement of the paper (surface strength; bursting strength; tensile strength), the degraded amylopectin potato starch derivatives give equivalent or better results compared with corresponding derivatives based on other types of starch. The invention accordingly relates to a method for surface sizing paper wherein amylopectin potato starch granules isolated from potato tubers obtained from genetically modified potato plants which form said starch granules in the potato tubers, said starch granules comprising more than 95 % by weight, based on dry substance, of amylopectin, are degraded and wherein an aqueous solution of the degraded amylopectin potato starch is applied to the paper, whereafter the sized paper is dried.

[0013] For use with the method according to the invention, it is essential that the starch is partially depolymerized. Partial depolymerisation of the amylopectin potato starch reduces the viscosity of the starch solution used, which enables the use of starch solutions having an increased dry matter content compared with solutions of non-degraded starch. The partial depolymerization of the starch also enhances its ability to penetrate between the cellulose fibers and to bind the surface fibers together.

[0014] There are various methods for degrading starch, in which use can be made of oxidants, acids and/or enzymes. The degradation can take place at the starch manufacturer's, whereby typically an oxidized or acid-degraded ungelatinized, granular starch product is obtained, which is gelatinized in the paper factory. The degradation of the starch can also be carried out in the paper factory, whereby the starch, typically in gelatinized condition, is treated with enzymes (enzymatic conversion) or with oxidants (thermal chemical conversion). The extent of degradation is dependent on the starting starch material, the operating conditions during surface sizing and the desired paper properties.

[0015] Before, during or after the degradation reaction, the amylopectin potato starch can additionally be modified chemically by esterification or etherification. The invention further comprises the use of additionally modified degraded amylopectin potato starch derivatives.

[0016] The viscosity of the solutions of degraded amylopectin potato starch to be used according to the invention is preferably between 4 and 1000 mPa.s and most preferably between 10 and 100 mPa.s, measured with a Brookfield viscosimeter (type LVT at 60 rpm) at a dry matter concentration of the starch of 8% by weight and a temperature of 35°C.

[0017] The solutions of degraded amylopectin potato starch can be applied to paper or paperboard using the known application techniques. In these techniques, application equipment with presses, grooved rolls and calender sets are used. Thus, for instance, with a size press the surface sizing is performed in that the sheet of paper is guided between a pair of pressing rolls, with the lower roll of the pair rotating in a bath with the starch solution. The surface of this roll entrains the size and applies it to the underside of the paper sheet. If desired, the starch solution can also be applied to the top side of the paper sheet, to which effect the starch solution is sprayed into the slit between the paper sheet and the upper roll or against the upper roll, so that the starch solution is disposed on the top side of the paper sheet as it enters the press.

[0018] Regardless of how the starch solution is applied in the size press, the paper sheet is passed between rolls in

order to drive the starch solution into the paper and also to remove excess starch solution. The distance between the size press rolls is set in such a manner that the rolls exert sufficient pressure to control the penetration of the starch solution into the paper. Thereafter the surface sized paper sheets are dried.

[0019] If desired, the degraded amylopectin potato starch can also be applied to the paper sheet utilizing an air knife, a trailing knife, a champion knife or a calender.

[0020] The starch concentration of the starch solution to be applied to the paper sheet can vary between 2 and 20% by weight. The amount of starch product which is applied can vary between 0.25 and 15% by weight of starch, calculated as dry substance with respect to the dry weight of the paper (SW52).

[0021] The invention is further explained and illustrated in and by the following examples.

Example 1

[0022] In this example, degraded potato starch (containing about 80% amylopectin), degraded waxy maize starch (containing more than 95% amylopectin) and degraded amylopectin potato starch (containing more than 95% amylopectin) of comparable viscosity were compared with each other with regard to the use as surface sizing agent for paper.

[0023] Potato starch, waxy maize starch and amylopectin potato starch were gelatinized and degraded (converted) to a comparable viscosity. The conversion was carried out continuously in a so-called jet cooker (steam injection device) with hydrogen peroxide (as oxidant) at a starch concentration of 30% by weight (in water) and a boiling temperature of 140°C. This method of conversion is referred to as thermochemical conversion. The aqueous solution of degraded starch flowing from the jet cooker was diluted with water to a starch concentration of 8% by weight. The viscosity of the starch solution obtained (containing 8% by weight of starch) was measured with a Brookfield viscosimeter (type LVT) at 60 rpm and a temperature of 35°C. This viscosity was 8 mPa.s for all three types of degraded starch (potato starch, waxy maize starch, and amylopectin potato starch).

[0024] The starch solutions (8% by weight of starch; temperature 50°C) were applied to a base paper (type Van Gelder) using a horizontal size press (type T.H. Dixon; model 160-B; roll hardness 80 shore). The machine speed of the Dixon was 50 m/min and the line pressure was 7 kg/cm. The surface sized paper was thereafter dried to 5% by weight of moisture. The paper samples obtained were conditioned at 23°C and 50% relative humidity.

[0025] With the test methods specified below, the properties of the surface sized paper were determined:

Property	Apparatus	Test method
Sheet weight	Balance	NEN 1109
Porosity	Gurley L § W type 6/2	NEN 2016
Bursting strength	Lorentzen § Wettre type 14-1	NEN 1765
Tensile strength	Adamel Lhomargy type DY-20 Serial number 160	NEN 1249
IGT dry pick	IGT AIC 2-5 IGT AE	NEN 3095 Tappi 51

[0026] In Table 1 below, the following designations are used:

AZM	potato starch
WMZM	waxy maize starch
AAZM	amylopectin potato starch
ZZ	wire side
VZ	felt side

(continued)

MR	machine direction
DR	cross direction

[0027] Table 1 specifies the paper properties obtained when using degraded potato starch (AZM-1), degraded waxy maize starch (WMZM-1) and degraded amylopectin potato starch (AAZM-1).

TABLE 1

Paper properties								
Starch	Starch content Wt. %	Sheet weight g/m^2	Porosity Gurley s/ 100ml	Bursting strength	IGT dry pick		Tensile strength kN/m	
				kN/m^2	ZZ	VZ	MR	DR
AZM-1	3.3	74.5	29	250	2860	1770	5.1	2.5
WMZM-1	3.2	74.3	28	242	2880	2100	4.9	2.3
AAZM-1	3.3	75.0	32	262	4860	3270	5.3	2.5

[0028] It appears from Table 1 that the surface strength, measured with the dry pick test, when using degraded amylopectin potato starch (AAZM-1) gives clearly better values than when using degraded potato starch (AZM-1) or degraded waxy maize starch (WMZM-1). Also with regard to the bursting strength, degraded amylopectin potato starch gives the best results.

Example 2

[0029] In the same manner as described in Example 1, surface sized papers were produced. In this case, however, less far degraded starches were used. The viscosity of the starch solutions to be used (containing 8% by weight of starch) was measured with a Brookfield viscosimeter (type LVT) at 60 rpm and a temperature of 35°C. This viscosity was comparable for the three starch solutions and was 16 mPa.s for degraded potato starch (AZM-2), 14 mPa.s for degraded waxy maize starch (WMZM-2) and 17 mPa.s for degraded amylopectin potato starch (AAZM-2). The paper properties of the surface sized papers are shown in Table 2.

TABLE 2

Paper properties								
Starch	Starch content Wt. %	Sheet weight g/m^2	Porosity Gurley s/ 100ml	Bursting strength kN/m^2	IGT dry pick		Tensile strength kN/m	
					ZZ	VZ	MR	DR
AZM-2	3.4	74.3	35	254	2670	1970	5.5	2.5
WMZM-2	3.4	74.0	28	255	2970	2390	5.5	2.3
AAZM-2	3.5	75.8	35	263	3330	3010	5.8	2.4

[0030] From Table 2 too it appears that the surface strength, measured with the dry pick test, gives clearly better values when using degraded amylopectin potato starch (AAZM-2) than when using degraded potato starch (AZM-2) or degraded waxy maize starch (WMZM-2). Also with regard to bursting strength, degraded amylopectin potato starch gives the best results.

Claims

1. A method for surface sizing paper wherein amylopectin potato starch granules isolated from potato tubers obtained from genetically modified potato plants which form said starch granules in the potato tubers, said starch granules comprising more than 95 % by weight, based on dry substance, of amylopectin, are degraded, and wherein an

aqueous solution of the degraded amylopectin potato starch is applied to the paper and the sized paper is thereafter dried.

2. A method according to claim 1, **characterized in that** the amylopectin starch has been isolated from potatoes originating from potato plants obtained through mutation.

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

4. A method according claims 1-3, **characterized in that** the viscosity of the aqueous solution of the degraded amylopectin potato starch is between 4 and 1000 mPas, measured with a Brookfield viscosimeter (type LVT; at 60 rpm) at a starch concentration of 8% by weight and at a temperature of 35 °C.

5. A method according claims 1-3, **characterized in that** the viscosity of the aqueous solution of the degraded amylopectin potato starch is between 10 and 100 mPas, measured with a Brookfield viscosimeter (type LVT; at 60 rpm) at a starch concentration of 8% by weight and at a temperature of 35 °C.

Patentansprüche

1. Verfahren zum Oberflächenleimen von Papier, bei dem Amylopektin-Kartoffelstärke-Körnchen degradiert werden, die von Kartoffelknollen isoliert wurden, welche aus genetisch modifizierten Kartoffelpflanzen erhalten wurden, die die Stärkekörnchen in den Kartoffelknollen bilden, wobei die Stärkekörnchen Amylopektin in einem Gewichtsanteil von mehr als 95% basierend auf Trockensubstanz enthalten, und bei dem eine wässrige Lösung der degradierten Amylopektin-Kartoffelstärke auf das Papier aufgebracht wird und das geleimte Papier anschließend getrocknet wird.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Amylopektin-Stärke aus Kartoffeln isoliert worden ist, die von durch Mutation erhaltenen Kartoffelpflanzen stammt.

3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Amylopektin-Stärke aus Kartoffeln isoliert worden ist, die von durch Antisense-Inhibition erhaltenen Kartoffelpflanzen stammt.

4. Verfahren nach einem der Ansprüche 1-3, **dadurch gekennzeichnet, dass** die Viskosität der wässrigen Lösung der degradierten Amylopektin-Kartoffelstärke zwischen 4 und 1000 mPas liegt, gemessen mit einem Brookfield-Viskosimeter (Typ LVT; bei 60 U/min.) bei einer Stärkekonzentration von 8 Gewichts-% und bei einer Temperatur von 35°.

5. Verfahren nach einem der Ansprüche 1-3, **dadurch gekennzeichnet, dass** die Viskosität der wässrigen Lösung der degradierten Amylopektin-Kartoffelstärke zwischen 10 und 100 mPas liegt, gemessen mit einem Brookfield-Viskosimeter (Typ LVT; bei 60 U/min.) bei einer Stärkekonzentration von 8 Gewichts-% und bei einer Temperatur von 35°.

Revendications

1. Procédé de collage en surface de papier dans lequel des granules de fécule de pomme de terre à base d'amylopectine isolés à partir de tubercules de pomme de terre obtenus à partir de plants de pomme de terre génétiquement modifiés qui forment lesdits granules de fécule dans les tubercules de pomme de terre, lesdits granules d'amidon comprenant plus de 95% en poids, en de fécule sèche, d'amylopectine, sont dégradés, et dans lequel une solution aqueuse de la fécule de pomme de terre à base d'amylopectine dégradée est appliquée sur le papier, après quoi le papier collé est séché.

2. Procédé selon la revendication 1, **caractérisé en ce que** la fécule d'amylopectine a été isolée de pommes de terre provenant de plants de pommes de terre obtenus au moyen d'une mutation.

3. Procédé selon la revendication 1, **caractérisé en ce que** la fécule d'amylopectine a été isolée de pommes de terre provenant de plants de pomme de terre obtenus au moyen d'une inhibition anti-sens.

4. Procédé selon les revendications 1 à 3, **caractérisé en ce que** la viscosité de la solution aqueuse de la fécule de pommes de terre d'amylopectine dégradée est comprise entre 4 et 1 000 mPa.s mesurée avec un viscosimètre Brookfield (type LVT ; à 60 tr/mn) avec une concentration en fécule de 8% en poids et à une température de 35°C.

5. Procédé selon les revendications 1 à 3, **caractérisé en ce que** la viscosité de la solution aqueuse de la fécule de pommes de terre d'amylopectine dégradée est comprise entre 10 et 100 mPa.s mesurée avec un viscosimètre Brookfield (type LVT ; à 60 tr/mn) avec une concentration en fécule de 8% en poids et à une température de 35°C.

REFERENCES CITED IN THE DESCRIPTION

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