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(54) A process for surface sizing or coating paper

(57) The invention relates to a process for surface-sizing and/or coating paper, wherein an aqueous size or coating liquid is used which contains converted starch which has been obtained by treating gelatinized starch or a gelatinized modified starch in aqueous medium with a starch-converting enzyme selected from the group of the cyclodextrin glycosyl transferases (EC 2.4.1.19) and the branching enzymes (EC 2.4.1.18). The invention further relates to a process of preparing a converted aqueous starch solution by carrying out a treatment as indicated above.

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Description

This invention relates to a process for surface sizing or coating paper. The surface sizing of paper is a coating treatment which serves to make the surface of paper sufficiently smooth and strong, *inter alia* to improve the writing quality of the paper. In the coating of paper, the paper surface is provided with a layer of pigment, which serves *inter alia* to obtain a glossy and well printable surface.

In the two above-mentioned applications it is not possible to use native starch or non-decomposed modified starch as binding agent because the viscosity of these starch products upon gelatinization is too high. It has therefore been proposed to depolymerize the starch molecules partially. Conventional depolymerization methods for starch are oxidation and enzymatic conversion with α-amylase (GB-A-871,937, Example 6). However, progressive depolymerization of the starch molecules also has as a result that desired properties, such as the film strength and the binding force, are reduced increasingly. Moreover, in the enzymatic conversion of amylase-containing kinds of starch with α-amylase, starch solutions are obtained which are not viscostable. In fact, upon storage the viscosity of these solutions increases, which is mainly caused by the presence of amylase molecules that retrograde. As a result, in the course of time these starch solutions exhibit retrogradation phenomena, such as viscosity increase, turbidity, gelling and precipitation.

In order to counteract these retrogradation phenomena, it is possible to start from types of starch that do not contain amylose, the so-called amylopectin starch types. Also usable as starting material are starch esters or starch ethers, which exhibit a lesser tendency to retrograde owing to the introduction of substituents into the amylose molecules. Further, it is possible to add to the starch certain additives which increase the viscostability of the starch solutions. However, appropriately modifying starch is laborious, while the addition of additives results in starch solutions having a more complex composition. In addition, the reagents used for etherifying or esterifying starch, the by-products formed in the process and/or the additives used may be undesirable with respect to toxicity and the environment.

A first object of the invention is to provide a process as described in the preamble, in which an aqueous size or coating liquid is used which possesses a reduced and stable viscosity, so that that liquid can be used readily and reliably for a long time.

Another object of the invention is to provide such a process which yields a surface size layer or coating layer with a good film strength and binding force.

Yet another object of the invention is to provide a process for surface sizing paper, in which an aqueous size liquid is used in such a manner that an increase of the starch retention is effected or that, given the same starch retention, greater ease of handling and processability of the size liquid are achieved.

Still another object of the invention is to provide a process for coating paper, in which an aqueous coating liquid is used which also contains a high concentration of pigment particles in suspension, that coating liquid possessing an improved rheology.

The object of the invention is also to provide a process for preparing a converted (reduced viscosity) starch solution which is suitable for surface sizing or coating paper.

Further objects of the invention will appear from the following description.

To achieve the objects of the invention, for the purpose of surface sizing or coating paper, use is made of an aqueous size or coating liquid which contains converted starch which has been obtained by treating gelatinized starch or a gelatinized modified starch in aqueous medium with a starch-converting enzyme selected from the group of the cyclodextrin glycosyl transferases (EC 2.4.1.19) and the branching enzymes (EC 2.4.1.18).

Cyclodextrin glycosyl transferases (EC 2.4.1.19), CGT enzyme for short, are enzymes which via an exomechanism are capable of splitting off ring-shaped cyclodextrin molecules (having 6, 7 or 8 glucose units) from starch molecules. Branching enzymes (EC 2.4.1.18) are enzymes capable of converting α-1,4-glycosidic bonds in starch molecules to an α-1,6-bond. CGT enzyme and branching enzyme belong to the starch-converting enzymes, whereby during the conversion the reducing capacity of the starch product is not increased or is increased only to a very minor extent. The action of CGT enzymes and branching enzymes on gelatinized starch leads to a reduction of the viscosity without the high-molecular character of the starch decreasing to a corresponding extent. The established stability of the condition thus achieved contributes considerably to the realization of the above-indicated objects of the invention.

As starting material for obtaining the converted starch to be used in accordance with the invention, all native (unmodified) starch types can be used, such as potato starch (which may contain 20 to 100 % by weight amylopectin), maize starch, wheat starch, tapioca starch or waxy maize starch. With particular advantage amylose-containing starches are used. Also usable as starting material are modified starches, such as starch esters, starch ethers, including cationic starch, and cross-linked starch.

The employed cyclodextrin glycosyl transferase (EC 2.4.1.19) can originate from different sources, such as described in the following publications:
R.L. Whistler, J.N. Bemiller, E.F. Paschall (Eds) Starch: Chemistry and Technology, Second Edition, 1984, Academic Press, pp. 143-144; D. Duchêne (Ed), Minutes of the Fifth International Symposium on Cyclodextrins, Editions de Santé, Paris 1990, pp. 19-61; and A.R. Hedges (Ed), Minutes of the Sixth International Symposium on Cyclodextrins, Editions

de Santé, Paris 1992, pp. 23-58. European patent specification 0,418,945 describes processes for obtaining branching enzymes (EC 2.4.1.18).

For an effective action of the CGT-enzyme or the branching enzyme on the starch molecules, the starch must be in gelatinized condition. The gelatinization of the starch can be carried out batchwise or continuously in a steam injection device (jet-cookers). The enzyme can be added before or after the gelatinization. In a preferred embodiment, the starch, in the form of a suspension, wet cake or dry product, is first mixed in the desired ratio with the enzyme preparation and, if necessary, dried. The dried mixed product (compound) can then be mixed with water in the paper factory, whereafter the starch is gelatinized and the conversion is carried out to obtain a converted starch solution for use in surface sizing or coating paper in accordance with the invention.

The conversion conditions (concentrations, temperature, pH, time) can vary within wide limits and depend in particular on the starting material, the enzyme, the origin of the enzyme and the desired extent of conversion. Suitable conditions are mentioned in the patent specifications mentioned hereinbefore. After the conversion has progressed to the desired extent, the enzyme used can be inactivated, for instance by increasing the temperature of the conversion mass. If desired, the converted starch solution obtained can be diluted with water to the desired processing concentration for surface sizing or coating paper. (SW49).

The invention is further explained in and by the following Examples. In these Examples, a number of chemically modified starches are used for comparison, viz.:

Oxidized starch A: obtained by oxidation of potato starch with sodium hypochlorite (low viscosity)

Oxidized starch B: obtained by oxidation of potato starch with sodium hypochlorite (medium to low viscosity)

Oxidized starch C: obtained by oxidation of potato starch with sodium hypochlorite (high viscosity)

Hydroxyethyl starch A: obtained by reacting oxidized potato starch (low viscosity) with ethylene oxide to an MS (molar substitution) of 0.07.

Hydroxyethyl starch B: obtained by reacting oxidized potato starch (medium viscosity) with ethylene oxide to an MS of 0.11.

Hydroxyethyl starch C: obtained by reacting oxidized potato starch (medium viscosity) with ethylene oxide to an MS of 0.07.

The following enzymes are mentioned in the Examples: α-amylase: enzyme preparation Novoban 240.

CGT-enzyme: cyclodextrin glycosyl transferase (EC 2.4.1.19)

Branching enzyme (EC 2.4.1.18): enzyme preparation obtained according to European patent specification 0,418,945.

The degree of branching of a starch product was determined by measuring the DE (Dextrose Equivalent) of the starch product after debranching with the enzyme iso-amylase. The higher the DE (after debranching), the higher the degree of branching. Upon debranching, potato starch gives a DE of 5. The additional branching effected by the branching enzyme according to the invention is calculated as:

$$\text{Additional \% branching} = \frac{\text{DE} - 5}{5} \times 100\%$$

The additionally branched starch was prepared by treating an aqueous solution of potato starch with a branching enzyme preparation. This treatment took place at 50°C for 16 hours. The reaction was discontinued by heating to 100°C. Then the starch solution was purified by means of filtration. The filtrate was then sprayed-dried to a dry additionally branched starch product.

The viscosity of the starch solutions was determined with a Brookfield viscosimeter, type LVT.

The properties of the surface-sized paper and the coated paper were determined with the following test methods.

PAPER TEST	APPARATUS/MATERIALS	TEST METHODS
Brightness	Elropho 2000	NEN 1843
Whiteness	datacolor	Tappi 452
Gloss	Novo Gloss	Tappi 480
Porosity	Bekk, type 131 ED	NEN 2014
Porosity	Gurley, L & W type 6/2	NEN 2016
Smoothness	Bekk, type 131 ED	Tappi 479
Bursting strength	Lorentzen & Wettre type 14-1	NEN 1765
Stiffness Kodak Pathé	Adamel Lhomargy type RM-01	NEN 1840
IGT pick resistance	IGT AIC 2-5	NEN 3095 Tappi 514
Dry pick	Prüfbau printability tester type MZ-1	Standard Avebe
Wet rub test	Adams Spectronic 20 Bausch & Lomb	Avebe-report 83171-330033
K & N ink penetration	Lorilleus inkt Elrepho 2000 datacolor	IGT W 25
CMT-30	Grüneweald Fluter No. 3212	Tappi 809 SU 1966
Water retention	AAGWR gravimetry	Instructions supplier
Starch pick up	Spectrophotometer 330 nm	Hexokinase method acc. to Böhringer
Micro mottle	IGT AIC 2-5	Acc. to KNP instructions.

Example 1

In this Example the viscostability of CGT-enzyme converted starch solutions (potato starch and maize starch) is compared with the viscostability of α-amylase converted starch solutions (potato starch and maize starch) and of solutions of oxidized starch (potato starch and maize starch).

The CGT-enzyme converted starch solutions were produced as follows. To a suspension of starch in water (30% by weight of starch) was added 0.5% by weight (based on dry substance) of a CGT-enzyme preparation. This suspension was heated with direct steam (3°C per minute) to 75°C, whereafter the starch solution obtained was maintained at 75°C for 10 minutes. The converted starch solution obtained was then passed through a steam injection device (jet-cooker), where the CGT-enzyme was inactivated at 140°C for 45 seconds. The starch solution obtained was then diluted with water to approximately 20% by weight of dry substance and cooled to 50°C. The viscostability of these starch solutions was determined by measuring the viscosities (Brookfield, type LVT, 30 rpm) directly upon the preparation of the solution and subsequently after 1, 2, 4 and 24 hours' storage in an oven.

The α-amylase converted starch solutions were produced as follows. To a suspension of starch in water (30% by weight starch) was added 0.025% by weight (based on dry substance) of an α-amylase preparation. This suspension was heated with direct steam (3°C per minute) to 75°C. Then the converted starch solution obtained was passed through a jet-cooker, where the enzyme was inactivated at 140°C for 45 seconds. The further treatment was the same as described above for the starch solutions converted with CGT-enzyme.

The aqueous solutions of oxidized starch were prepared as follows. A suspension of oxidized starch (potato starch, maize starch) in water (35% by weight dry substance) was passed through a jet-cooker at 110°C (potato starch) or 140°C (maize starch). The thus obtained solution of oxidized starch was then diluted with water to approximately 20% by weight of dry substance and cooled to 50°C. The viscostability was measured as mentioned for the CGT-enzyme converted starch solution.

The results obtained are shown in Table 1 for potato starch and in Table 2 for maize starch.

Table 1

Viscostability (mPa.s) of converted potato starch solutions at 50°C.			
viscosity	CGT-converted 19.0 wt.% d.s.	α-amylase converted 20.3 wt.% d.s.	oxidized 19.7 wt.% d.s.
direct	175	150	120
after 1 h.	190	1300	350
after 2 h.	203	gel	2200
after 4 h.	195	gel	gel
after 24 h.	195	gel	gel

From Table 1 it appears that the potato starch solution converted with CGT-enzyme is much stabler in viscosity, in comparison with corresponding solutions of α-amylase converted potato starch and oxidized potato starch. By gel formation the viscosity becomes so high that the measuring method used is rendered useless.

Table 2

Viscostability (mPa.s) of converted maize starch solutions at 50°C.			
viscosity	CGT-converted 19.5 wt.% d.s.	α-amylase converted 21.5 wt.% d.s.	oxidized 19.2 wt.% d.s.
direct	220	120	190
after 1 h.	340	290	gel
after 2 h.	420	1140	gel
after 4 h.	475	3250	gel
after 24 h.	630	gel	gel

From Table 2 it appears that the maize starch solution converted with CGT-enzyme is much stabler in viscosity in comparison with corresponding solutions of α-amylase converted maize starch and oxidized maize starch.

Example 2

In this Example the following three starch products are compared with respect to their use as surface sizing agent for paper:

a) CGT-enzyme converted potato starch solution produced as described in Example 1.
b) Hydroxyethyl starch A (as described above).
c) Hydroxyethyl starch C (as described above).

These starch products were applied to a base paper (fluting from paper factory De Hoop) in the form of an aqueous solution by means of a horizontal size press (type T.H. Dixon; model 160-B; roll hardness 80 shore). The surface-sized paper was then dried with an air foil drier to a moisture content of 5% by weight. Table 3 shows the starch concentration (% by weight) and the Brookfield viscosity of the starch solutions to be applied to the base paper. Table 3 further specifies a number of relevant properties of the dried surface-sized paper obtained.

Table 3

Surface sizing of paper						
Starch product	Concentration %	Viscosity mPa.s 50°C	Starch pick up %	Bursting strength kPa	Stiffness mN.m	CMT-30 N
CGT-converted starch	8.1	10	2.2	215	3.5	190
Hydroxyethyl starch A	7.8	8	2.0	205	3.5	170
Hydroxyethyl starch B	3.9	10	1.2	170	3.4	160

From Table 3 it appears that when CGT-converted potato starch is used, a higher CMT-30 is obtained than if the two types of hydroxyethyl starches are used. As for the bursting strength and stiffness, CGT-converted potato starch gives equivalent or better results in comparison with the hydroxyethyl starches.

Example 3

In this Example the following three starch products are compared with respect to the use as surface sizing agent for paper:

a) Additionally branched potato starch (additional branching 10%) obtained by the action of a branching enzyme on gelatinized potato starch (as described above)
b) α-amylase converted potato starch (as described above in Example 1)
c) α-amylase converted waxy maize starch (as described in Example 1 for potato starch).

These three starch products were applied as aqueous solutions to NCR base paper (manufacturer Wiggins Teape Virginal) by means of a horizontal size press (Dixon). The surface-sized paper was then dried with an air foil dryer to a moisture content of 5% by weight. Table 4 summarizes the starch concentration (in % by weight) and the Brookfield viscosity (at 50°C) of the starch solutions to be applied to the base paper. Table 4 further specifies a number of relevant properties of the dried surface-sized paper obtained.

Table 4

Surface-sizing of paper

Starch product	Concentration %	Viscosity mPa.s 50°C	Starch pick up %	Bursting strength kPa	IGT VVP	Porosity s/100 ml	Stiffness mN.m
Addionally branched potato starch	6.3	7	2.1	175	1375	15	0.24
	9	10	3.2	195	1500	17	0.24
Alpha-amylase converted potato starch	5.3	14	2.3	175	1350	16	0.24
Alpha-amylase	5.6	13.5	2.2	165	1175	16	0.24

From Table 4 it appears that when additionally branched potato starch is used (despite the low viscosity), the paper properties are comparable with α-amylase converted potato starch and are better than α-amalyse converted waxy maize starch. Due to the lower viscosity level of solutions of branched starch, the processability (flow behaviour) in the size press is better than in the case of the two α-amylase converted starches.

Example 4

In this Example, three CGT-enzyme converted potato starch products (produced as described in Example 1) of different viscosity levels are compared with three types of hydroxyethyl starch (with corresponding viscosity levels) as binding agent in paper coating. Table 5 specifies the viscosity of the coating binders.

Table 5

Viscosity of coating binding agents		
Starch product	Starch concentration in wt.%	Brookfield-viscosity at 50°C in mPa.s
a) CGT-converted potato starch	18	58
b) CGT-converted potato starch	18.5	290
c) CGT-converted potato starch	18.3	760
d) Hydroxyethyl starch A	18	49
e) Hydroxyethyl starch B	18.5	245
f) Hydroxyetyhl starch C	18.6	820

Table 6 specifies the basic formulation which is used to prepare the coating composition.

Table 6

Coating composition	
Component	Parts by weight
CPS-clay	100
Starch product (see table 5)	6
Dow 935 (Dow Chemical)	6
Blancophor P (BASF)	0.3
BIP BC 336 (BIP) (hardener)	1
Dispex N40 (Allied Colloids)	0.3
Water to 54-58 wt.% dry substance	

Table 7 specifies the properties of the coating composition to be applied to paper (at 25-26°C and a pH of 8.0).

Table 7

Properties of coating composition			
Starch product	Viscosity 100 rpm mPa.s	Hi-shear Viscosity 1100 rpm mPa.s	Dry substance % by weight
a) CGT-converted potato starch	800	52	57.30
b) CGT-converted potato starch	1240	87	56.14
c) CGT-converted potato starch	1560	95	54.30
d) Hydroxyethyl starch A	790	57	57.45
e) Hydroxyethyl starch B	1200	94	56.39
f) Hydroxyethyl starch C	1480	113	54.72

This coating composition was applied to a fine-grade coating base paper (80 g/m^2; manufacturer Nymölla), using a puddle type blade (Jagenberg; 50 m/min.) of the Dixon (approximately 15 g/m^2). The coated paper was dried to 5% by weight of moisture by means of an air foil dryer on the Dixon. The coated papers were calendered by means of a laboratory calender at 50°C, 50 kg pressure and 2 nips. The paper samples obtained were conditioned and tested at

23°C and 50% relative humidity. The properties of the coated papers are specified in Table 8.

Table 8

Properties of coated paper

Starch product	Sheet weight g/m^2	Brightness Elrepho %	Gloss %	Porosity Bekk $ml/s/cm^2$	Smoothness Bekk s/10 ml	IGT pick resistance VVP	Dry pick Prüfbau m/s	Wet rub. test %
a) CGT-converted potato starch	90.3	95.0	42.6	0.29	240.1	450	0.23	69
b) CGT-converted potato starch	89.5	94.3	43.9	0.22	259.0	550	0.29	67
c) CGT-converted potato starch	91.2	95.1	45.5	0.17	296.1	590	0.35	87
d) Hydroxyethyl starch B	89.2	95.5	43.4	0.30	245.9	520	0.12	51
e) Hydroxyethyl starch B	90.8	95.5	45.6	0.22	302.7	610	0.31	65
f) Hydroxyethyl starch C	91.0	94.7	45.2	0.13	413.3	810	0.41	61

Table 9 is a qualitative presentation of a number of test results of the coated paper.
The qualitative indications have the following meaning:

-	means: lower values;
+	means: good values;
++	means: higher values.

Table 9

Qualitative summary of test results

Property	CGT-converted a	CGT-converted b	CGT-converted c	Hydroxy-ethyl starch A	Hydroxy-ethyl starch B	Hydroxy-ethyl starch C
Viscosity level	low	medium	high	low	medium	high
Coating properties	+	+	+	+	+	+
Porosity	++	++	++	+	+	+
Gloss	+	+	+	+	+	++
Smoothness	+	+	+	+	+	++
Wet rub	++	+	++	+	+	+
K & N	+	+	+	-	-	-
Micro mottle	+	+	+	-	-	-

Example 5

In this Example the following starch products are compared as binders in paper coatings (in a precoat composition):

a) Additionally branched potato starch (with 110% additional branching) of a viscosity of 210 mPa.s in an aqueous solution of 42% by weight of dry substance.
b) An oxidized potato starch having a viscosity of 250 mPa.s in an aqueous solution of 42% by weight of dry substance.

The coating composition contained 100 parts by weight of SPS-clay, 12.5 parts by weight of starch product and water. Table 10 shows the properties of the coating composition.

Table 10

Properties coating composition		
Properties	Additionally branched potato starch	Oxidized potato starch
Dry substance %	70.3	69.1
Water retention gr 0.5/1.5 kg/cm^2	5/5	5/20
Brookfield 100 rpm, mPa.s	1160	1520
Hi-shear, 1100 rpm, mPa.s	332	247
Brookfield after 24 h. mPa.s	1040	1880

The coating composition was applied to a fine-grade coating base paper (80g/m^2; manufacturer Nymölla), using a puddle type blade (Jagenberg; speed 50 m/min.) of the Dixon (approximately 10 g/m^2). The coated paper was dried to 5% by weight of moisture. The paper samples were conditioned and tested at 23°C and 50% relative humidity. The properties of the coated papers are shown in Table 11.

Table 11

Properties of coated papers		
Properties	Additionally branched potato starch	Oxidized potato starch
Whiteness %	108.1	107.6
Smoothness sec/10 ml	27.4	26.6
Porosity	3.1	2.6
IGT-pick VVP	960	1010
Prüfbau pick	>3	>3

Claims

1. A process for surface-sizing and/or coating paper, characterized in that an aqueous size or coating liquid is used which contains converted starch which has been obtained by treating gelatinized starch or a gelatinized modified starch in aqueous medium with a starch-converting enzyme selected from the group of the cyclodextrin glycosyl transferases (EC 2.4.1.19) and the branching enzymes (EC 2.4.1.18).

2. A process according to claim 1, characterized in that as starting material, native starch is used.

3. A process according to claim 1, characterized in that as starting material, a modified starch is used.

4. A process according to claims 1-3, characterized in that the starch or the modified starch is first mixed with the enzyme and the dry mixed product is then gelatinized in water.

5. A process according to claims 1-4, characterized in that the aqueous medium in which the starch conversion is carried out is used as such in the size or coating liquid for paper.

6. A process according to claims 1-5, characterized in that the binding agent of the aqueous size or coating liquid consists wholly or partly of the converted starch.

7. A process according to claims 1-6, characterized in that an aqueous size liquid is used in such a manner that an increase of the starch retention during surface-sizing is effected or that, given the same starch retention, greater ease of handling and processability of the aqueous size liquid are achieved.

8. A process according to claims 1-6, characterized in that an aqueous coating liquid is used which also contains a high concentration of pigment particles in suspension, said coating liquid possessing an improved rheology because of the presence of the converted starch.

9. A process for preparing a converted aqueous starch solution, characterized in that gelatinized starch or a gelatinized modified starch is treated in aqueous medium with a starch-converting enzyme selected from the group of the cyclodextrin glycosyl transferases (EC 2.4.1.19) and the branching enzymes (EC 2.4.1.18).

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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 1751

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)
A	GB-A-871 937 (O.J.MEIJERS) * claims 1-11 * -----	1-9	D21H19/54 D21H17/28 D21H17/29
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			D21H C12N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 September 1995	Fouquier, J-P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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