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(54) **A process for surface sizing or coating paper**

Verfahren zum Leimen der Oberfläche und zum Streichen von Papier

Procédé pour encoller en surface et revêtir du papier

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Description

[0001] 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.

[0002] 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.

[0003] 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.

[0004] 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.

[0005] 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.

[0006] 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.

[0007] 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.

[0008] Further objects of the invention will appear from the following description.

[0009] 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 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) or by treating a gelatinized starch or a gelatinized modified starch in aqueous medium with a starch-converting enzyme selected from the group of the branching enzymes (EC 2.4.1.18).

[0010] 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, as for example described in WO89/01043 or WO92/13962. 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.

[0011] As starting material for obtaining the converted starch to be used in accordance with claim 1 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 in accordance with claims 1 and 2 are modified starches, such as starch esters, starch ethers, including cationic starch, and cross-linked starch.

[0012] 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 Inter-

national 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).

[0013] 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.

[0014] 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).

[0015] 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.

[0016] 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.

[0017] 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:

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

[0018] 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.

[0019] The viscosity of the starch solutions was determined with a Brookfield viscosimeter, type LVT.

[0020] 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	Adamel Lhomargy	NEN 1840

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PAPER TEST	APPARATUS/ MATERIALS	TEST METHODS
Kodak Pathé	type RM-01	
IGT pick resistance	IGT AIC 2-5	NEN 3095 Tappl 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 Böhlinger
Micro mottle	IGT AIC 2-5	Acc. to KNP instructions.

Example 1

[0021] In this Example the following three starch products are compared with respect to the use as surface sizing agent for paper:

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

[0022] 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.

[0023] These three starch 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 1

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
Additionally 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

[0024] From Table 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 -amylase 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 2

[0025] 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.

[0026] The coating composition contained 100 parts by weight of SPS-clay, 12.5 parts by weight of starch product and water. Table 2 shows the properties of the coating composition.

Table 2

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

[0027] The coating composition was applied to a fine-grade coating base paper (80g/m²; manufacturer Nymölla), using a puddle type blade (Jagenberg; speed 50 m/min.) of the Dixon (approximately 10 g/m²). 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 3.

Table 3

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, wherein an aqueous size or coating liquid is used which contains converted starch which has been obtained by treating gelatinised starch or a gelatinised modified starch in an aqueous medium with a starch-converting enzyme selected from the group of the branching enzymes (EC 2.4.1.18).
2. 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 gelatinised modified starch in an aqueous medium with a starch-converting enzyme selected from the group of the cyclodextrin glycosyl transferases (EC 2.4.1.19).
3. A process according to claim 1, wherein as starting material native starch is used.

4. A process according to claim 1, wherein as starting material a modified starch is used.
5. A process according to any of the preceding claims, wherein the starch or modified starch is first mixed with the enzyme and the dry mixed product is then gelatinised in water.
6. A process according to any of the preceding claims, wherein the aqueous medium in which the starch conversion is carried out is used as such in the size or coating liquid for paper.
7. A process according to any of the preceding claims, wherein the binding agent of the aqueous size or coating liquid consists wholly or partly of the converted starch.
8. A process according to any of the preceding claims, wherein an aqueous size liquid is used in such a manner that an increase of the starch uptake during surface-sizing is effected or that, given the same starch retention, greater ease of handling and processability of the aqueous size liquid is achieved.
9. A process according to any of the claims 1-7, wherein 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.

Patentansprüche

1. Verfahren zum Leimen der Oberfläche und/oder zum Streichen von Papier, **dadurch gekennzeichnet, dass** eine wässrige Leim- oder Streichflüssigkeit verwendet wird, welche umgewandelte Stärke enthält, die durch Behandlung gelatinierter Stärke oder gelatinierter modifizierter Stärke in einem wässrigen Medium mit einem stärkeumwandelnden Enzym erhalten worden ist, das aus der Gruppe aus verzweigenden Enzymen (EC 2.4.1.18) ausgewählt ist.
2. Verfahren zum Leimen der Oberfläche und/oder zum Streichen von Papier, **dadurch gekennzeichnet, dass** eine wässrige Leim- oder Streichflüssigkeit verwendet wird, welche umgewandelte Stärke enthält, die durch Behandlung gelatinierter Stärke oder gelatinierter modifizierter Stärke in einem wässrigen Medium mit einem stärkeumwandelnden Enzym erhalten worden ist, das aus der Gruppe aus Cyclodextringlycosyltransferasen (EC 2.4.1.19) ausgewählt ist.
3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** native Stärke als Ausgangsmaterial verwendet wird.
4. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** modifizierte Stärke als Ausgangsmaterial verwendet wird.
5. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** die gegebenenfalls modifizierte Stärke zunächst mit dem Enzym vermischt und das trockene Mischprodukt danach in Wasser gelatinisiert wird.
6. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** das wässrige Medium, in welchem die Stärkeumwandlung durchgeführt wird, als solches in der Leim- oder Streichflüssigkeit für Papier verwendet wird.
7. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** das Bindemittel der wässrigen Leim- oder Streichflüssigkeit ganz oder teilweise aus der umgewandelten Stärke besteht.
8. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** eine wässrige Leimflüssigkeit derart verwendet wird, dass während des Leimens der Oberfläche eine Vergrößerung der Stärkeaufnahme erfolgt oder bei gleicher Stärkeaufnahme eine leichtere Handhabung und Verarbeitbarkeit der wässrigen Leimflüssigkeit erreicht wird.
9. Verfahren nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, dass** eine wässrige Streichflüssigkeit verwendet wird, die auch eine hohe Konzentration an Pigmentteilchen suspendiert enthält, wobei die Streichflüssigkeit wegen des Vorhandenseins der umgewandelten Stärke ein verbessertes Fließverhalten besitzt.

Revendications

1. Procédé pour l'encollage en surface et/ou le couchage de papier, dans lequel un encollage aqueux ou un liquide de couchage est utilisé qui contient de l'amidon converti que l'on a obtenu en traitant un amidon gélatinisé ou un amidon modifié gélatinisé dans un milieu aqueux avec une enzyme, convertissant l'amidon, choisie dans le groupe des enzymes de ramification (EC 2.4.1.18).
2. Procédé pour l'encollage en surface et/ou le couchage de papier, dans lequel un encollage aqueux ou un liquide de couchage est utilisé, qui contient un amidon converti qui a été obtenu en traitant un amidon modifié gélatinisé dans un milieu aqueux avec une enzyme, convertissant l'amidon, choisie dans le groupe des cyclodextrine glycosyltransférases (EC 2.4.1.19).
3. Procédé selon la revendication 1, dans lequel, comme matière de départ, on utilise un amidon d'origine naturelle.
4. Procédé selon la revendication 1, dans lequel, comme matière de départ, on utilise un amidon modifié.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'amidon ou l'amidon modifié est d'abord mélangé avec l'enzyme et le produit mélangé sec est ensuite gélatinisé dans l'eau.
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le milieu aqueux dans lequel la conversion de l'amidon est réalisée, est utilisé tel quel dans l'encollage ou le liquide de couchage pour papier.
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'agent de liaison de l'encollage aqueux ou du liquide de couchage se compose entièrement ou partiellement de l'amidon converti.
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le liquide d'encollage aqueux est utilisé de telle manière qu'une augmentation de la prise de l'amidon pendant l'encollage en surface est réalisé ou que, pour une même rétention d'amidon donné, une facilité plus grande de manipulation et d'aptitude au traitement du liquide d'encollage aqueux est réalisée.
9. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel un liquide de couchage aqueux est utilisé qui contient également une concentration élevée de particules de pigments en suspension, ledit liquide de couchage possédant une rhéologie améliorée à cause de la présence de l'amidon converti.