Title: AMYLOSE STARCH PRODUCTS AS SIZING AGENTS FOR TEXTILE YARNS

Abstract: The invention relates to the use of chemically unmodified amyllose-type starch products as sizing agent for sizing natural and/or synthetic yarns. The invention also relates to a process for sizing natural and/or synthetic yarns using chemically modified amyllose-type starch products as sizing agent.

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Amylose starch products as sizing agents for textile yarns

Description

The invention relates to the use of native chemically unmodified amylose-type starch as sizing agent for natural and/or synthetic textile yarns and textile blended yarns as well as to a process for sizing textile yarns using these starch products. The invention furthermore relates to the use of chemically modified amylose-type starch as sizing agent for natural and/or synthetic textile yarns and textile blended yarns as well as to a process for sizing textile yarns using chemically modified amylose-type starch products.

Woven fabrics are two-dimensional bodies consisting of fibers in the form of threads intersecting at right angles (the warp and weft), produced using the shed-forming method. Whereas each weft thread is stressed only briefly as it is placed in position, the warp threads undergo repeated stress during each insertion of the weft and at each change of shed. The warp threads undergo stress in the form of yarn – metal abrasion when the weft thread is pushed by the reed, by yarn – yarn abrasion during the change of shed, and by cyclic stretching processes. The warp threads are normally unable to withstand these extreme stresses, and must therefore be provided with a protective coating – the sizing agent – that adheres to the fiber, forming an abrasion-resistant, elastic film. With staple fiber yarns, the sizing agents have the task of making the yarn resistant to the frictional processes that take place during weaving. Protruding fibers are caused to adhere to the main body of the yarn, thereby preventing neighboring warp threads from catching or entangling. The overall increase in the tensile strength of the thread of about 20 % is of minor importance, but the increase in strength at the weakest points is crucial.

The sizing agent must adhere strongly to the fiber, and its film properties should be largely independent of the climatic conditions, especially atmospheric humidity, and be unaffected by fiber finishes and sizing additives. The elongation of the warp thread should not be reduced by presence of the sizing agent.

After the gray cloth has been woven, the task of the sizing agent is complete. As it would usually have a deleterious effect on subsequent finishing processes, it must be completely removed. Removal is simple in the case of cold-water-soluble sizing agents, but starch products that are insoluble in cold water require preliminary enzymatic or oxidative breakdown before the desizing stage. The removal of the sizing agent may pose special wastewater treatment problems in finishing plants.
A large number of classes of chemical substances are used as sizing agents. They can be divided into two main groups.

1) Macromolecular natural products and their derivatives: starches and starch derivatives, carboxymethyl cellulose, galactomannan, and tamarind flour derivatives

2) Synthetic polymers: poly(vinyl alcohol), poly(meth)acrylates, polyester condensates, and polyvinyl compounds

The growth of synthetic fibers and the developments in weaving technology have accelerated the development of synthetic sizing agents.

The sizing agent to be used must satisfy different requirements, such as good penetrativeness, good adhesiveness, good film-forming properties and the ability to form an elastic sizing film. A suitable sizing agent imparts to the sized yarn desirable properties, such as a high wear resistance (abrasion resistance), a high weaving efficiency and good washing-out properties of the woven textile product.

About 70% of the consumption of sizing agents worldwide are starches and starch derivatives.

Starch and its derivatives are therefore the most important class of sizing agents with respect to total consumption. This is because of their low price, good sizing effect, and worldwide availability. The raw material basis of this class of sizing materials is naturally occurring starch, a polysaccharide based on α-D-glucopyranose. Starch is not a single chemical substance, but is composed of two structurally different polymers: amylase and amylpectin. Amylose consists of chains of glucose units linked by α-1,4-glucosidic bonds, whereas amylpectin additionally contains α-1,6-glucosidic bonds which cause branching of the polymer chain, see J.A. Radley: Starch and its Derivatives, Chapman & Hall, London 1968; M.W. Rutenberg in R.L. Davidson (ed.): Handbook of Water-Soluble Gums and Resins, McGraw-Hill, New York 1980, chap. 22; J. BeMiller in R.L. Whistler, J.N. BeMiller (eds.): Industrial Gums, Academic Press, San Diego 1993, p. 579; G. Tegge: Stärke und Stärkederivate, Behr's Verlag, Hamburg 1984.

Amylopectin is the main constituent of starch, making up 73 to 86 % of the total, depending on the type of starch. The degree of polymerisation of amylpectin is about 6000 to $10^8$ glucose units, that of amylase about 100 to 1000 glucose units.
The most important sizing agents are potato, maize, and tapioca starches. Wheat, rice, and sago starches are also used. The characteristic properties of these starches are determined by the amylose/amylopectin ratio, the degree of polymerization of these two constituents, and the size and fine structure of the starch grain. These parameters determine the swelling and solution behavior, and also the properties of the film.

Natural starch is insoluble in cold water because of the hydrogen bonds linking parallel polymer chains. The starch is brought into "solution" by heating. The starch grains first absorb water until swelling is at its maximum. Above a certain temperature, characteristic for each type of starch and known as the gelatinization temperature, the starch grains burst and form a gel. The viscosity increases to a maximum, and then decreases asymptotically to a limiting value as the solubilized polymer molecules disperse. Complete solubilization of the individual molecules of a starch grain only occurs above 100°C. The viscosity value is important in size application, as it has a considerable effect on the amount of liquor pickup.

On storage and with decreasing temperature, starch pastes solidify to a pulpy mass. This retrogradation is caused by stretching of the molecular chains, parallel alignment of the chains, and formation of hydrogen bonds between neighboring chains, with loss of water of hydration (Tegge, 1984). This retrogradation has detrimental effects on the sizing agent, leading to poor storage properties, skin formation, formation of deposits on the rollers, and reduced adhesive strength. Therefore, natural starches are increasingly being replaced by starch derivatives.

Native potato starch e.g. consists of about 80% amylopectin (I) and 20% amylose (II).

\[ \text{(I)} \quad \text{Representative structure of amylopectin, including (1,6)-\(\alpha\)-D branch point} \]
Both polymers are present in granules, which are insoluble in water at room temperature. Upon heating a starch suspension, the hydrogen bonds between the amylopectin and amylose chains become weaker and are finally replaced by interactions (hydrogen bonds) with water molecules. Starting from about 61°C the granules start to swell and water molecules penetrate into the starch. Once in solution amylopectin is viscosity stable, while amylose has a high tendency to gel. During this gel formation the amylose forms double helices, which then aggregate and form threedimensional networks.

The use of the various chemically modified starch products as sizing agents for textile yarns has been extensively described by K.W. Kirby; Textile Industry, in the book by O.B. Wurzburg (Ed.): Modified Starches: Properties and Uses CRC Press Inc. Boca Raton, Florida, 1986, pages 229-252. Mentioned as chemically modified starches are: acid-modified starch, oxidized starch, crosslinked starch, starch ethers and starch esters. As starting material for the modification, the various types of starch may be used, such as maize starch, potato starch, tapioca starch and wheat starch.

It is well known that starches are useful in sizing cotton fibers and for a wide variety of other industrial purposes. In recent years, many synthetic fibers have become available, and it has been difficult to find relatively inexpensive sizing compositions which are suitable for sizing a wide variety of these fibers, including mixtures of cotton and synthetic fibers. In particular, it has been difficult to provide suitable low cost sizing compositions for mixtures of polyester fibers and cotton. In common practice, the fibers are sized in the form of threads or yarns prior to weaving. The sized threads or yarns are then woven into cloth and thereafter the sizing material is removed by washing with water containing detergent or by treatment with enzymes. A satisfactory sizing composition is one which will provide suitable lubrication and resistance during weaving and at the same time can be readily removed thereafter.

All modified starches that have lost their original properties are referred to as starch derivatives. These include thin-boiling starches, dextrins, starch esters, and starch ethers.

Thin-boiling starches are produced by acid hydrolysis or oxidative degradation in aqueous suspension, and dextrins are produced by thermal depolymerization, usually
in the presence of acids. They gelatinize at low temperatures, give solutions of low viscosity, and can be dissolved in high concentrations. Furthermore, it is easier to produce a liquor with a predetermined viscosity, and the tendency to retrogradation is considerably reduced.

The starch esters mainly used in sizing materials are those of phosphoric acid (the phosphate starches) and acetic acid (the acetyl starches). These starch derivatives are usually not only esterified, but also depolymerized, giving lower liquor viscosities and decreased retrogradation. In general, they give better sizing effects than thin-boiling starches.

The three most important types of starch ethers are the hydroxyethyl, hydroxypropyl, and carboxymethyl starches, produced by reaction of starch with ethylene oxide, propylene oxide, and chloracetic acid or sodium chloroacetate in the presence of caustic soda, respectively. The degree of substitution of these starch derivatives is generally about 0.1 or less. Because of its ionic character, sodium carboxymethyl starch is soluble in cold water and therefore does not require enzymatic desizing. Also, the starch ethers have a better sizing effect than starch derivatives that are simply depolymerized.

The mechanical properties of films cast from solutions of starch or starch derivatives depend on the degree of hydration (which depends on the relative humidity of the atmosphere in the weaving mill) and on the ratio of amyllose to amyllopectin and type of modified starch.

The main use of starch and starch derivatives is for sizing yarns of pure cotton and its blends with other fibers. For these yarns, a large number of sizing formulations are used which consist either exclusively or principally of starch or starch derivatives. Starch and its derivatives adhere relatively strongly to cotton, see J. Trauter, M. Laupichler, *Melliland Textilber. 57* (1976) 375, 443, 545, 615, 713, 797, 875, 979; 58 (1977) 23, 111. J. Trauter, H. Bauer, B. Rueß, M. Laupichler, *Textilbetrieb (Würzburg)*, 96 (1978) 46; J. Trauter, *TPI Text. Prax. Int.* 44 (1989) 1297. Cotton yarns woven on high-speed looms or yarn blends with a high proportion of synthetic fiber must be sized with sizing formulations that contain additionally carboxymethyl cellulose, poly(vinyl alcohol), or poly(meth)-acrylates to improve the sizing effect. Starches are detected by the blue coloration with iodine, and this reaction is also used for the semiquantitative determination of residual size content (P. Wurster, G. Schmidt, *Melliland Textilber. 68* (1987) 581).

It is an object of the present invention to provide a sizing agent on the basis of chemically unmodified amylose-type starch that gives very favorable sizing properties, weaving properties of the sized yarn and washing-out properties of the woven cloth.
Furthermore it is an object of this invention to provide a sizing agent wherein the amylose-type starch is chemically modified.

According to the invention this object is achieved by using amylose-type starch with an amylose content of at least 50 % as sizing agent.

Amylose type potato starch with an amylose content of about 70 % produced by transgenic potato plants as described in example 1 was formulated as described in example 2 and tested as sizing agent as described in example 3. Furthermore the desizing properties were analysed, see example 3.

Compared to the conventional potato starch, the formulations with amylose-type starch from genetically modified potato plants produced as described in example 1 and having an amylose content of about 70 % display a significant increase in sizing performance as reflected from the higher abrasion resistance as well as the better desizing properties achieved. Compared to the best commercially available reference sample, which was already chemically modified and optimised, comparable properties with chemically unmodified amylose-type starch were obtained.

The term "high amylose starch" refers to any starch or starch fraction containing at least about 50 % by weight amylose. Exemplary thereof are "Nepol" amylose (the amylose fraction of corn starch); "Superlose" (the amylose fraction of potato starch); "Amylomaize" or Amylon (high amylosic corn starch with about 54 % amylose); and Amylomaize VII (high amylose corn starch containing about 73.3 % amylose). Amylomaize VIII with an amylose content of around 85 % can also be used. The starch can be of any origin, for example, corn, wheat, potato, waxy corn, tapioca, sago or rice.

In the sizing of textile fibers a typical sizing composition can be prepared by mixing 100 pounds of an amphoteric starch prepared in accordance with this invention with 100 gallons of water, preferably with the addition of five pounds of petroleum wax, and then heating to the gelatinization temperature. The thread or yarn to be sized, for example, a thread or yarn containing 65 % polyester fiber (polyethylene glycol terephthalate), and 35 % cotton fibers, is then sized by passing it through this composition. In using this sizing composition, the number of yards of woven material between changes of loom stops can be increased.

After weaving, the sizing material can be removed by treatment with enzymes in the usual manner or by washing with a detergent water.
The compositions of the invention can also be employed in other uses, for example, in the finishing of textiles, in dyeing textiles and paper, in the sizing of paper, in the application of pigments or coatings to cloth and paper.

Sizing of 65% polyethylene glycol terephthalate, 35% combed cotton yarn, rayons, and yarns of other synthetic fibers or blends thereof with e.g. but not limited to natural fibers, such as cotton, wool can be carried out by using amylose-type starch with an amylose content of at least 50% as sizing agent according to the invention.

Due to its linearity, amylose has the potential to form flexible films, with excellent functionality for sizing of yarns. Important is to prevent gelling in this process, because this will lead to insoluble films and shrinking due to crystallisation. Therefore amylose is substituted with hydroxyethyl-, hydroxypropyl- or carboxymethyl groups, so that amorphous, highly soluble films result or amylose is mixed with poly(meth)acrylate sizes to prevent retrogradation after the usual cooking procedure.

It has been found that the objective can be achieved according to the invention preferably by using chemically unmodified or modified amylose-type potato starch as sizing agent for natural and/or synthetic textile yarns. Hereinafter follows a brief characterization about amylose-type potato starch.

The potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylpectin (wt.%, based on the dry substance). In the past 10 years, however, successful efforts have been made to breed, through genetic modification, potato plants that form starch granules in the potato tubers, which consist as to more than 50 wt.% (based on the dry substance) of amylose, preferably more than 70 wt.% of amylose, most preferably more than 90 wt.% of amylose.

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 a gene that codes for the GBSS enzyme. Elimination or inhibition of the expression of the specific genes starch branching enzyme 1 (SBE1) and starch branching enzyme 2 (SBE2) of amylpectin biosynthesis result in a complete loss or in an inhibition of amylpectin biosynthesis in e.g. potato plants. The elimination of these genes can be realized preferably by genetic modification of potato plant material.

Elimination or inhibition of the expression of the SBE1 and SBE2 genes in potato plants especially in the tubers is also possible by the use of antisense technology, see example 1. The method of genetic modification of the potato has been described in the patent applications WO92/11375, WO 97/20040, WO 92/14827, WO 95/26407.

By application of genetic modification it has been found possible to breed and grow potatoes the starch granules of which contain little or substantially no amylopectin.

The term amylose-type potato starch is herein understood to mean the potato starch granules isolated from potato tubers, having an amylose content of at least 50 wt.% based on the dry substance.

Chemically modified amylose-type starches are herein understood to mean amylose-type starch products obtained by chemically modifying amylose-type starch through acid modification, oxidation, esterification, etherification, graft polymerization and/or crosslinking. Before, during or after the chemical modification a physical modification (for instance, through roller drying, extrusion or a heat-moisture treatment) or an enzymatic modification of the amylose-type starch may also be carried out. Methods for preparing the various chemically modified starches have been described in the book O.B. Wurzburg (Ed. Modified Starches: Properties and Uses; CRC Press Inc. Boca Raton, Florida, 1986. These methods can also be used for preparing chemically modified amylose-type potato starch used according to the invention as sizing agent.

Aqueous solutions of amylose-type starch as sizing agents, also referred to as sizing bath or sizing paste, may be made in the conventional manner, for instance in open or closed boiling apparatus. The treatment of the textile yarns with the aqueous solutions of chemically modified amylose-type potato starch products according to the invention can be carried out by the methods conventional for sizing yarns. The yarns can, for instance, be passed continuously through a solution of the sizing agent, or a solution of the sizing agent may be applied to the yarn by spraying or by means of a roller. After passing the sizing paste, the layer of yarn is pressed out, for instance between two rollers. Then the pressed-out yarns are dried on heated cylinders or by means of hot air.

It has been found that chemically modified amylose-type starch is very suitable as sizing agent for textile yarns. The yarns sized according to the invention are well-resistant to mechanical influences (high shear resistance) in that they are coated with a strong, elastic, smooth covering. In the weaving mill, excellent results are obtained with these yarns (high weaving efficiency).

As stated before, the invention relates to a process for sizing textile yarns. In this connection, the term yarns is herein understood in the most general sense and is deemed to comprise all cotton threads or cotton staple yarns occurring in the textile
industry. They may consist of continuous natural cotton threads or of cotton fibers and/or semisynthetic cotton and polyester blends and be twisted or not twisted.

The invention will be further explained in and by the following examples. According to the examples the sized yarns have been examined for some characteristic properties.

In the sizing of textile fibers a typical sizing composition can be prepared by mixing 100 pounds of an amphoteric starch prepared in accordance with this invention with 100 gallons of water, preferably with the addition of five pounds of petroleum wax, and then heating to the gelatinization temperature. The thread or yarn to be sized, for example, a thread or yarn containing 65% polyester fiber (polyethylene glycol terephthalate) and 35% cotton fibers, is then sized by passing it through this composition.

An alternative sizing agent can be prepared by adding neutralized (e.g. with ammonia or sodium hydroxide) poly(meth)acrylate-based emulsion polymers to the starch containing sizing formulation. A preferred copolymer composition (weight %) of the poly(meth)acrylate polymers is in the range of:

\[
\begin{align*}
0 &- 10\% \text{ acrylic acid} \\
0 &- 20\% \text{ methacrylic acid} \\
10 &- 20\% \text{ acrylonitrile} \\
0 &- 25\% \text{ ethylacrylate} \\
0 &- 60\% \text{ butylacrylate} \\
20 &- 70\% \text{ methylacrylate}
\end{align*}
\]

To obtain a good penetration of the sizing agent into the yarn, the sizing bath is preferably kept at a temperature of from 30 to 90°C. The concentration of the sizing agent in the sizing bath is preferably between 2 and 20 wt.%. The amount of sizing agent absorbed by the yarn (absorption; weighting) is preferably between 2 and 30 wt.% of sizing agent (dry substance) based on yarn (dry substance). Besides the chemically modified amylose-type potato starch, the sizing solutions to be used may further contain slight amounts of auxiliary substances conventional in the sizing process, such as waxes, fats, antifoaming agents, antistatic agents and plasticizers. The sizing solutions may additionally contain other sizing agents, such as polyvinyl alcohol, poly(meth)acrylates or carboxymethyl cellulose.

In using this sizing composition, the number of yards of woven material between changes of loom stops can be increased. After weaving, the sizing material can be removed by treatment with enzymes in the usual manner or by washing with a detergent water.
The compositions of the invention can also be employed in other uses, for example, in the finishing of textiles, in dyeing textiles and paper, in the sizing of paper, in the application of pigments or coatings to cloth and paper.

Example 1

**Transgenic potato plant Solanum tuberosum AM 99-2003**

High amylose potato lines can be produced for example by using antisense, RNAi or antibody technology that target the two starch branching enzymes starch branching enzyme 1 (SBE1) and starch branching enzyme 2 (SBE2).

The high amylose potato line AM99-2003 is produced by inhibition of the starch branching enzyme activities in the parental line Dinamo. Transformation is made with a construct of SBE1 and SBE2 in antisense orientation driven by the gbss promoter. The nucleic acid sequence of the gbss promoter is published in EP 0 563 189.

pBluescript containing a 1620bp fragment of the 3'end of Sbe1 between EcoRV and SpeI is cut open with SpeI (blunt) and Xbal and ligated with a 1243bp SstI (blunt) and Xbal fragment of the 3'end of Sbe2. The Sbe2 and Sbe1 complex is cut cut with EcoRV and Xbal and ligated to the Smal and Xbal opened up binary vector pHo3.1. The final vector is named pHabe12A, see figure 1 and nucleic acid sequence SEQ ID NO 1. pHo3.1 is based on pGPTVkan (Becker, D. et al., Plant Molecular Biology 20 (1992), 1195-1197) with the addition of the 987bp gbss promoter cloned at the HindIII site of pGPTVkan and the uidA gene is deleted by Smal and SstI.

The parental line Dinamo is transformed with the construct pHabe12A and transgenic lines were selected as described in US 6,169,226. Transgenic lines were grown and analysed for amylose production according to the method as described by Morrison, W.R. and Laignelet, B., J. Cereal Sci. 1(1983), 9-20. Transgenic lines producing amylose-type starch with an amylose content of 70% and more were selected. Amylose type starch was isolated and purified from transgenic potato plants according to common methods known in starch industry.

Example 2

**Formulation**

For the sizing experiments, a formulation containing the above mentioned amylose-type potato starch was produced according to the following recipe:
The amounts of the individual components of the formulation can hereby vary as follows:

Depending on the required performance in weaving, the above recipe of size liquor can principally vary from 100% starch (low performance required) to 100% poly(meth)acrylate (high performance required). Normally for compromise between cost and performance, poly(meth)acrylate based size is added to starch size in a ratio between 10 (starch):1 (poly(meth)acrylate) to 1:1.

Example 3

Testing

In a comparative test, the above described amylose-type starch (recipe 1: PHAS 2012) was tested against native potato starch (recipe 2) as well as against the best commercially available starch-sizing-product (recipe 3: Emsize E9), which is based on a chemically modified starch (propoxylated, degree 0.2 to 0.3/per repeating unit). All starch
components were formulated with "BASF size CE". The abrasion resistance and the desizing properties were determined.

The tests were performed according to the following procedure:

5 Abrasion test

The sizing effect is of decisive importance for the weaving properties of a warp yarn. This effect is closely connected with the abrasion resistance of the sized yarn. We determine the abrasion resistance of the yarn with the Zweigle abrasion tester (G552 abrasion tester, Zweigle Textilprüfmaschinen GmbH & Co. KG, Germany).

A standard, readily exchangeable abrasive paper is tensioned over a shaft that moves in line with the direction of the threads. Twenty, weighted threads (cotton staple yarn English count Ne12) are laid over the shaft and abraded at the same speed and under the same pressure until they break. To ensure that fibrous deposits in the abrasive do not affect the abrasive action, the shaft is advanced after each stroke. The number of abrasive strokes withstands before breaking is read off from a counter, and the average figure calculated. The higher the abrasion number obtained, the higher the abrasion resistance of the yarn.

The figures obtained on the abrasion tester are only relative, they must be considered in comparison with unsized warp yarn or with warp yarn sized with another recipe, in both cases from the same lot.

The following results were obtained:

Abrasion account numbers (cotton yarn, Ne 12)

<table>
<thead>
<tr>
<th>Recipe</th>
<th>unsized</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size loading (solid to solid, %)</td>
<td></td>
<td>7,7</td>
<td>7,6</td>
<td>7,5</td>
</tr>
<tr>
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<td></td>
<td>263</td>
<td>1752</td>
<td>1416</td>
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<td>Abrasion account number (5)</td>
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<td>1001</td>
<td>868</td>
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Desizing test

Detection of starch by TEGEWA method

One of the commonest test methods for determining the effect of pretreatment is to detect the presence of starch sizes by dabbing the fabric with a solution of iodine/potassium iodide. A blue coloration indicates that starch size is still present on the fabric.
In the application of this test, it is important to know that even if only 1 % of the original starch size is still present, i.e. if 99 % has been removed, a blue coloration will still be visible. However, this slight amount of residual size will certainly no longer have any influence on the behaviour of the pretreated goods during dyeing or printing.

A remedy is offered by the TEGEWA violet scale, which embraces nine shades denoted by ratings. A rating of 1 indicates poorest desizing; and of 9 practically complete desizing.

Procedure

Immerse a specimen of the fabric for one minute in a 0.005 mol/l iodine solution. Afterwards wash briefly in water, dab with filter paper, and compare immediately with the violet scale.

Preparation of the iodine solution

1. Dissolve 10 g of potassium iodide in 100 ml of distilled water
2. Add and dissolve 0.635 g of iodine in this solution
3. Make up to 800 ml with water
4. Make up to 1000 ml with ethanol

Desizing properties

<table>
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<th>Recipe</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>Size washed off in 5 min. (%)</td>
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</tr>
<tr>
<td>Size washed off in 10 min. (%)</td>
<td>76,3</td>
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<td>77,3</td>
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<tr>
<td>Size washed off in 30 min. (%)</td>
<td>96,5</td>
<td>76,8</td>
<td>95,5</td>
</tr>
<tr>
<td>TEGEWA 5 min.</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TEGEWA 10 min.</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>TEGEWA 30 min.</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Compared to the conventional potato starch, the formulations with amylose-type starch from genetically modified potato plants produced as described in example 1 and having an amylose content of about 70 % display a significant increase in sizing performance as reflected from the higher abrasion resistance as well as the better desizing properties achieved. Compared to the best commercially available reference sample, which was already chemically modified and optimised, comparable properties with the chemically unmodified amylose-type starch were obtained.
Claims

1. Method of using amylose-type starch as sizing agent for natural cotton yarn.

2. Method of using amylose-type starch as sizing agent according to claim 1 characterized in that the amylose-type starch has an amylose content of at least 50%.

3. Method of using amylose-type starch as sizing agent according to claim 2 characterized in that the amylose-type starch is produced by transgenic potato plants.

4. Method of using amylose-type starch as sizing agent according to claim 1, 2 or 3 characterized by using the amylose-type starch in combination with other sizing agents, such as polyvinyl alcohol, carboxymethyl cellulose or poly(meth)acrylate.

5. A process for sizing natural cotton yarn or blends of cotton and polyester yarn characterized by using chemically unmodified amylose-type starch as sizing agent.

6. A process for sizing natural cotton yarn or blends of cotton and polyester yarn characterized by using chemically modified amylose-type starch as sizing agent.

7. A process for sizing natural cotton yarn or blends of cotton and polyester yarn according to claims 5 or 6 characterized in that the amylose-type starch is produced by transgenic potato plants.

8. A process for sizing natural cotton yarn or blends of cotton and polyester yarn according to claim 7 characterized in that the amylose-type starch has an amylose content of at least 50%.
Figure 1

pHAbel2A
7756 bp
<110> BASF Plant Science GmbH

<120> Amylose starch product as sizing agents for textile sizing

<130> amylose as sizing agent

<140> EP20040190

<141> 2004-03-30

<160> 1

<170> PatentIn Ver. 2.1

<210> 1

<211> DNA

<220> Artificial Sequence

<223> Description of Artificial Sequence: vector phHabe12A

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ggcttctgct cgccggttgg ccagcggcag ccccttcgagc gttcgcgttc acgcgcacag 180

ggacacccgc tccaaatctg atagggcgttc ccctctatctg tcagcactct gcgcttcacag 240
tgcttagctg cggagctctg cggagctctg ccagctctctg ccagctctctg ccagctctctg 300

ggcacccggc ggagctctg ccagctctctg ccagctctctg ccagctctctg ccagctctctg 360

tgctctcttct gggctgct ggagctctg ccagctctctg ccagctctctg ccagctctctg 420

ggcacccggc ggagctctg ccagctctctg ccagctctctg ccagctctctg ccagctctctg 480

ggcagatgaag gaccaagtttt gggcgtgatt cccacaaagc gcggcggcag gttgctctgc 540

gcgcagcttc gcacagctgt ctctggggca gataagggcg ccagcccagc 600

ggcgcgagg ccacagcccg tggaggtctt aataacgtctg gacagcagcg tggaggtctt 660

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D06M15/11

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06M

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of box C.

Date of the actual completion of the international search 9 August 2005

Date of mailing of the international search report 17/08/2005

Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HM Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epoxy nl, Fax: (+31-70) 340-3016

Authorized officer Koegler-Hoffmann, S
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column 2, line 10 - line 16  
column 3, line 15 - line 49  
column 8, line 40 - line 75; claims | 1, 5, 6 |
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