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# METHOD OF SIZING TEXTILE YARNS

Jan Lolkema and Geert Moes, Hoogezand, and Willem Freerk Vogel, Groningen, Netherlands, assignors to W. A. Scholten's Chemische Fabrieken N.V., Groningen, Netherlands, a corporation of the Netherlands

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This invention relates to a method of sizing textile yarns. The term "yarns" is to be understood here in its widest sense and is considered to comprise all threads or yarns that occur in the textile industry. They may consist of continuous filaments or of fibers, may be of a natural, semi-synthetic or synthetic nature and may be twisted or untwisted.

In order to render textile yarns resistant against mechanical treatments it is customary to size the yarns prior to said mechanical treatments, for which purpose mostly aqueous solutions of sizing agents are used. The most generally known water soluble sizing agents used up to now are:

(1) Natural products on the basis of starch or protein.

(2) Derivatives of natural products on the basis of cellulose or starch.

(3) Synthetic sizing agents on the basis of polyvinyl alcohol, polyacrylic acid, polyacrylates and styrenemaleic acid derivatives.

For hydrophilic textile materials, such as cotton, wool or viscose rayon especially sizing agents from groups 1 and 2 are used. Strongly hydrophobic yarns, on the other hand, are preferably sized by means of products from group 3. Cellulose acetate yarns may be sized both with protein products and with synthetic agents.

We have now found that excellent results can be achieved if textile yarns are sized by treating them with an aqueous solution of water soluble ethers, esters or acetals of amylose, the yarns thus treated being subsequently dried. The effect obtained by sizing yarns with said amylose derivatives surprisingly not only in many respects exceeds the effect of the products from groups 1 and 2, but in addition they produce results that are at least just as good as results obtained by means of products from group 3.

The invention is more particularly of importance for sizing with amylose ethers and it will be therefore mainly described with reference to the use of the ethers.

As amylose ethers the water soluble alkyl ethers, hydroxyalkyl ethers and mixed alkyl and hydroxyalkyl ethers having 1–4 carbon atoms in the alkyl or hydroxyalkyl group are particularly suitable. The alkyl or hydroxyalkyl group should not be too large because otherwise the solutions of the amylose ethers in the concentration that is conventional for the sizing operation, e.g. 5–10%, show the tendency in the heat to form a skin at the surface. At least about 1 alkyl group or hydroxyalkyl group should be introduced per 7 anhydroglucose units of the amylose molecule in order to obtain products which form stable solutions both in the cold and in the heat, which is desirable for sizing solutions.

The above applies both to the amylose ethers to be used for sizing hydrophobic yarns and to the amylose ethers for sizing hydrophilic yarns. If hydroxyalkyl ethers are to be used for sizing hydrophobic yarns it is desirable to use a product of a higher degree of substitution, having e.g. 1 hydroxyalkyl group per 2½ anhydroglucose units. For this purpose alkyl ethers or hydroxyalkyl ethers which at the same time contain an aromatic group, e.g. ethylbenzyl ethers or hydroxyethylbenzyl ethers, are also suitable.



Amylose ethers containing hydrophilic groups in the substituent are especially eligible for sizing hydrophilic yarns. Examples of such ethers are the amylose ether carboxylic acids and amylose ether sulphonic acids, which can be used as such or in the form of their salts, e.g. the alkali salts. For this purpose also aminoalkyl ethers and aminoalkyl ethers substituted in the amino group are suitable.

The linear fraction obtained by separating starch into its components is preferably used as amylose raw material. The linear fraction may be used both in its pure and in its impure state and in many cases it offers advantages for the preparation of the amylose ethers to work up the linear fraction without an intermediate drying.

Instead of amylose preparations obtained by separating starch into its components it is also possible to use particular native starches having a high amylose content, e.g. starches of specific corn varieties.

The amylose ethers to be used according to the invention may be prepared by reacting the amylose with the etherifying agent in an aqueous medium in the presence of the required catalysts, more particularly alkaline substances, in the conventional manner. If desired, however, the etherification may also take place in an organic solvent.

It is possible, for example, to dissolve the amylose in water by heating at atmospheric or at elevated pressure, if desired, in the presence of substances having a peptisizing action and subsequently adding the desired amount of etherifying agent and, if necessary, the alkaline substance, whereupon the reaction is carried out at room temperature or at elevated temperature. The amylose ethers may be isolated from the reaction mixture, but this is not necessary. In many cases it is sufficient after the etherification of the amylose to dilute the reaction mixture with water to a concentration suitable for the sizing operation.

For actual practice it may be of importance to supply the amylose ethers in the form of dry products. Such dry products may be obtained by recovering the amylose ethers from the reaction mixture and purifying and subsequently drying them. However we have found that in most cases the isolation and purification of the ethers is not necessary and according to the invention dry products of very good properties may be obtained by drying the reaction mass in its entirety on heated rollers and grinding the film thus formed into flakes of the desired size. In this case care should be taken that the degree of substitution of the amylose ether is not so high that the mass will become plastic on the heated roller so that it would be difficult to remove it from the roller in the form of a thin film. As a rule difficulties of this nature will not manifest themselves e.g. in the case of alkyl ethers and hydroxyalkyl ethers unless the amylose ether contains more than one alkyl group and/or hydroxvalkyl group per anhydroglucose unit.

Suitable etherifying agents for the preparation of amylose alkyl ethers are i.e. the alkyl halides, dialkyl sulphates, alkyl tosylates and diazomethane. For the preparation of the hydroxyalkyl ethers alkylene oxides or alkylene chlorohydrins may be used.

For the preparation of the mixed ethers the amylose may be treated simultaneously or successively with the required etherifying agents.

The treatment of the yarns with aqueous solutions of amylose ethers according to the invention may be effected by conventional methods for sizing yarns. It is possible, for example, to submerge the yarns in the form of skeins in a solution of the sizing agent, to pass the yarns continuously through a solution of the sizing agent or to

apply a solution of the sizing agent to the yarn by spraying or by means of a roller. The yarns thus treated may be dried on heated drums or in heated drying chambers.

For obtaining a good penetration of the solution into the yarn the sizing bath is preferably kept at a temperature between 30 and 90° C. The concentration of the sizing solution may vary; very good results are obtained if said concentration is such that the yarn will absorb 2–10% of the dry sizing agent. The pH of the sizing solution may likewise vary within wide ranges; for sizing cellulose acetate yarns, the pH of the solution, however, should not exceed about 8.0. The sizing solutions to be used may contain in addition to the amylose ethers small amounts of the auxiliary agents conventionally used in sizing operations, for example softening agents, wetting agents or the like, but in general such auxiliary agents are unnecessary. In addition to the amylose ethers the solutions may also contain other sizing agents, if desired.

The yarns sized according to the invention are very resistent against mechanical influences, because they are coated with a strong, supple, smooth film. Especially in the weaving industry excellent results are obtained with said yarns. A further advantage of the use of said amylose ethers is that the yarns sized will not substantially take up a static charge. Furthermore they have the advantage that after the weaving operation they may easily be washed out from the yarns.

The invention has been described hereinbefore with reference to the use of water soluble amylose ethers. Instead of said ethers, however, water soluble amylose esters or amylose acetals may also be successfully used. Good results in sizing hydrophobic yarns are obtained, for example, by means of water soluble esters of amylose, which are derived from saturated or unsaturated fatty acids having not more than four carbon atoms, such as acetic acid, propionic acid, butyric acid, acrylic acid and methacrylic acid. For sizing hydrophilic yarns esters containing hydrophilic substituents are suitable, for example, amylose ester carboxylic acids and amylose ester sulphonic acids.

Suitable amylose acetals are those obtained by prepared reacting amylose with formaldehyde.

It is also possible to use amylose derivatives containing both ether groups and ester groups or amylose derivatives, which in addition to ether or esters groups contain acetal groups and may be obtained e.g. by reacting amylose ethers or amylose esters with formaldehyde. An example is an amylose benzyl ether which after the benzylation has been treated with formaldehyde.

The invention will be further elucidated with reference to some examples. According to said examples the yarns sized are tested for certain properties that are characteristic of the sizing effect obtained. The values mentioned in this connection have the following meaning:

The sizing value is a measure for the coherence of the elementary threads and as such it is very important. The first sizing value relates to the point at which the elementary threads become detached from each other, unstuck, the second value relates to the complete dislocation of the threads. A high value, therefore, is indicative of a good sizing. All of the values are the average of at least five observations.

The values for the breaking strength and the elongation are obtained according to conventional dynamometrical determinations.

The smoothness is expressed in the number of seconds which a thread of a specific length requires for passing an apparatus for determining the smoothness in the first and in the tenth passage respectively. Low values, therefore, are indicative of a high degree of smoothness.

The abrasion resistance is a measure for the resistance of the sized yarn against abrasion. A high value is indicative of a good abrasion resistance.



*Example 1*

A warp of acetate silk of 75 denier is continuously passed at a temperature of 60° C. through an 8% solution of an amylose ethyl ether (degree of substitution 0.40), whereupon the yarn is squeezed. The same test is made with a solution of an ethyl ether of tapioca starch of a corresponding degree of substitution. For purposes of comparison the same yarn is sized with a synthetic copolymer on styrene maleic acid anhydride basis, said copolymer being especially recommended for sizing acetate silk. The yarn is dried on drums at a temperature of from 80–90° C.

The following results are obtained:

| Sizing agent | Degree of substitution | Conc., percent | Sizing | Elongation, percent | Smoothness, sec. | |
|---|---|---|---|---|---|---|
| | | | | | 1st × | 10th × |
| amylose ethyl ether | 0.40 | 8 | 1.8–8.8 | 14.4 | 2.2 | 3.1 |
| starch ethyl ether | 0.40 | 8 | 1–3.2 | 14.9 | 2.7 | 2.9 |
| styrenemaleic acid anhydride copolymer | --- | 8 | 1.2–6.4 | 9.3 | 2.8 | 4.7 |

*Example 2*

A warp of acetate silk of 100 denier is sized at a temperature of 55° C. with aqueous solutions of some amylose alkyl ethers.

The results are as follows:

| Sizing agent | Degree of substitution | Conc., percent | Sizing | Elongation, percent | Smoothness, sec. | |
|---|---|---|---|---|---|---|
| | | | | | 1st × | 10th × |
| amylose methyl ether | 0.53 | 9.2 | 2–7.2 | 18.6 | 2.9 | 2.6 |
| amylose ethyl ether | 0.23 | 9.2 | 1.6–5.8 | 18.5 | 2.4 | 2.9 |
| amylose propyl ether | 0.19 | 9.2 | 2–5.6 | 18.8 | 3.0 | 3.8 |

*Example 3*

A warp of continuous nylon (on caprolactam basis) of 100 denier is sized at a temperature of 45° C. with an aqueous solution of an amylose ethyl ether (degree of substitution 0.40). For purposes of comparison this nylon is sized under the same conditions with a synthetic sizing agent on polymethacrylic acid basis, which is especially intended for sizing nylon. The sized yarn is dried on drums at 80–90° C. The results are as follows:

| Sizing agent | Degree of substitution | Conc., percent | Sizing | Elongation, percent | Smoothness, sec. | |
|---|---|---|---|---|---|---|
| | | | | | 1st × | 10th × |
| amylose ethyl ether | 0.40 | 9 | 2.8–13.2 | 29 | 2.4 | 2.8 |
| polymethacrylic acid | 0.40 | 9 | 2.6–15 | 26.4 | 2.1 | 2.3 |

The table shows that amylose ethyl ether produces about the same results as the polymethacrylic acid which is especially recommended for nylon, but is much more expensive than amylose ethyl ether.

*Example 4*

A hydroxypropyl ether of amylose with a degree of substitution of 0.51, a mixed ethylhydroxypropyl ether of amylose having a degree of substitution of 0.18 for the ethyl groups and of 0.30 for the hydroxyethyl groups, which two amylose ethers are excellently soluble both in cold and in hot water, and gelatin are used for sizing 75 denier acetate silk warps at a temperature of 60° C. To the solution of gelatin (which is frequently used for sizing acetate silk yarns in actual practice) a small amount of glycerol has been added.

When testing the yarns the following values for the sizing are obtained.

| Sizing agent | Degree of substitution | Concentration, percent | Sizing |
|---|---|---|---|
| amylose hydroxypropyl ether | 0.51 | 9 | 2–7.0 |
| amylose ethyl hydroxypropyl ether | 0.18+0.30 | 9 | 2.2–7.6 |
| gelatin (+ glycerol) | | 9 | 2–7.2 |

*Example 5*

A warp of cotton yarn Ne 24/1 is continuously passed at a temperature of 80° C. through a 10% sizing solution of an amylose ethyl ether (degree of substitution 0.30), squeezed out and dried on a drum at 110° C. For purposes of comparison the sizing test is also carried out with a thin boiling starch preparation, which in actual practice is frequently used in about the same concentration for sizing cotton.

The results of testing the yarn are as follows:

| Sizing agent | Conc., percent | Degree of substitution | Abrasion resistance | Breaking strength, grams | Elongation, percent |
|---|---|---|---|---|---|
| none | | | 84 | 269 | 7.2 |
| amylose ethyl ether | 10 | 0.30 | 1,144 | 420 | 6.1 |
| thin boiling starch | 10 | | 352 | 410 | 6 |

*Example 6*

In a closed dyeing apparatus a 4% solution of an amylose ethyl ether (degree of substitution 0.26) is pumped for 15 minutes at a temperature of 50° C. through a viscose spinning cake.

The sized spinning cake readily admits of being reeled off and the yarn has an excellent sizing.

*Example 7*

A skein of acetate silk of 100 denier is submerged for some minutes in a 9.2% solution of an amylose ethyl ether having a degree of substitution of 0.23 at a temperature of 60° C. After squeezing the skein and loosening the threads the skein is dried in a drying box at about 90° C. The sizing value of the yarn thus treated is found to be 1–6.8, the elongation is 25%.

*Example 8*

Continuous triacetate yarn of 100 denier is sized at a temperature of 50° C. with an aqueous solution of a water soluble mixed ethylbenzyl ether of amylose, obtained by treating amylose in an alkaline medium in the heat with 0.7 mole of diethyl sulphate and 0.05 mole of benzylchloride per glucose unit and by subsequently removing the reaction salts in known manner and bringing the mass in dry form. For purposes of comparison the sizing is also effected under the same conditions with a synthetic sizing agent on the basis of polyvinyl alcohol, in the presence of a slight amount of boric acid. After the treatment the yarn is dried on a drum at 95° C.

The following results are obtained:

| Sizing agent | Conc., percent | Sizing | Elongation., percent | Smoothness | |
|---|---|---|---|---|---|
| | | | | 1st × | 10th × |
| ethylbenzyl ether of amylose | 8 | 2.8–14.4 | 26.1 | 2.1 | 2.2 |
| polyvinyl alcohol – 1.6% of boric acid | 8 | 2.6–12.6 | 26.2 | 2.6 | 3.2 |

*Example 9*

The mixed ethylbenzyl ether of amylose described in Example 8 is compared with the corresponding ether of corn starch for sizing 75 denier diacetate silk warps at a



temperature of 60° C. The following sizing values are found.

| Sizing agent | Concentration, percent | Sizing |
|---|---|---|
| amylose ethylbenzyl ether | 9 | 1.8–9.2 |
| starch ethylbenzyl ether | 9 | 1.1–4.2 |

*Example 10*

Cotton yarn is continuously passed in warp form through a 10% aqueous solution of the sodium salt of a carboxymethyl ether of amylose at a temperature of 80° C., squeezed out and dried on a drum at 110° C.

The amylose ether is prepared by treating amylose in an alkaline medium in the heat with 1 mole of sodium monochloroacetate per glucose unit, whereupon the amylose thus treated is freed in known manner from the reaction salts, and is brought in dry form. The degree of substitution of the amylose ether is 0.56 carboxymethyl group per anhydroglucose unit. For purposes of comparison sizing tests are also run with a sodium salt of a carboxymethyl ether of cassava starch (degree of substitution 0.59), as well as with the sodium salt of a carboxymethyl cellulose of low viscosity (degree of substitution 0.6). The starch ether is obtained by etherifying cassava starch in known manner with one mole of sodium monochloroacetate per glucose unit and by subsequently removing the reaction salts.

The results of testing the yarn are as follows:

| Sizing agent | Conc., percent | Abrasion resistance | Breaking strength, grams | Elongation, percent |
|---|---|---|---|---|
| none | | 87 | 296 | 7.5 |
| carboxy-methyl ether of amylose (Na-salt) | 10 | 879 | 455 | 7.1 |
| carboxymethyl ether of starch (Na-salt) | 10 | 367 | 381 | 6.4 |
| carboxymethyl ether of cellulose (Na-salt) | 10 | 551 | 393 | 6.6 |

*Example 11*

A warp of diacetate silk of 75 denier is continuously passed through an 8% aqueous solution of amylose acetate at a temperature of 60° C., whereupon the yarn is squeezed out. The water soluble amylose acetate is obtained by hydrolyzing a solution of amylose triacetate in the presence of water and a small amount of a catalyst until the amylose acetate has become fully water soluble.

For purposes of comparison sizing tests are likewise carried out with water soluble starch acetate and water soluble cellulose acetate, said products being prepared in a similar way from the triacetates. The treated yarn is dried on drums at 80–90° C.

The results of the tests are as follows:

| Sizing agent | Conc., percent | Sizing | Elongation, percent | Smoothness | |
|---|---|---|---|---|---|
| | | | | 1st × | 10th × |
| amylose acetate | 8 | 2.7–9.4 | 17 | 1.9 | 2.1 |
| starch acetate | 8 | 1–3.4 | 12 | 2.7 | 5.2 |
| cellulose acetate | 8 | 1.2–5.0 | 15.5 | 2.4 | 3.7 |

*Example 12*

Cotton yarn is sized with a 10% aqueous solution of an amylose formaldehyde compound. The yarn thus sized is very suitable for weaving.

*Example 13*

A dry amylose ether to be used according to the invention having good properties may be prepared as follows:

In an autoclave provided with a stirring apparatus 1000

grams of finely ground amylose (obtained by fractionating potato starch) is agitated with a solution of 170 grams of sodium hydroxide in 2000 cc. of water at a temperature of 50–60° C., until a smooth dispersion is obtained. Subsequently 350 cc. of dimethyl sulphate are added in a period of 45 minutes, whereupon the mass is allowed to react for another hour at the same temperature. The reaction mixture is subsequently dried in a thin layer on a heated drum at a steam pressure of 6 at. The amylose methyl ether obtained has an excellent solubility both in cold and in hot water. The ether has a degree of substitution of 0.53 and accordingly contains 1 methyl group per 1.88 anhydroglucose units.

We claim:

1. In a method for sizing textile yarns, the improvement of treating said yarns with an aqueous solution of a sizing agent selected from the group consisting of amylose ethers, amylose esters, and amylose acetals, and subsequently drying the treated yarns.

2. The improvement described in claim 1, wherein said sizing agent is an alkyl ether of amylose, wherein each alkyl group has from 1 to 4 carbon atoms.

3. The improvement described in claim 2, wherein the sizing agent contains at least one alkyl group per 7 anhydroglucose units of the amylose.

4. The improvement described in claim 1, wherein said sizing agent is a hydroxyalkyl ether of amylose, wherein each hydroxyalkyl group has from 1 to 4 carbon atoms.

5. The improvement described in claim 4, wherein the sizing agent contains at least one hydroxyalkyl group per 7 anhydroglucose units of the amylose.

6. The improvement described in claim 1, wherein said sizing agent is a mixed alkyl hydroxyalkyl ether of amylose wherein each alkyl group has from 1 to 4 carbon atoms, and each hydroxy alkyl group has from 1 to 4 carbon atoms.



7. The improvement described in claim 1, wherein the textile yarns are hydrophobic yarns.

8. The improvement described in claim 7, wherein the sizing agent is a hydroxyalkyl ether of amylose containing at least one ether group per 2½ anhydroglucose units of the amylose.

9. The improvement described in claim 1, wherein the sizing agent is a mixed alkyl aryl ether of amylose.

10. The improvement described in claim 9, wherein the sizing agent is an ethyl benzyl ether of amylose.

11. The improvement described in claim 1, wherein the sizing agent is an ester of amylose and a fatty acid having from 2 to 4 carbon atoms.

12. The improvement described in claim 1, wherein said sizing agent is a carboxyalkyl ether of amylose, wherein the alkyl group has from 1 to 4 carbon atoms.

13. The improvement described in claim 1, wherein said sizing agent is a sulfoalkyl ether of amylose, wherein the alkyl group has from 1 to 4 carbon atoms.

14. The improvement described in claim 1, wherein said sizing agent is an aminoalkyl ether of amylose, wherein the alkyl group has from 1 to 4 carbon atoms.

15. The improvement described in claim 1, wherein said sizing agent is a substituted aminoalkyl ether of amylose, wherein the alkyl group has from 1 to 4 carbon atoms.

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