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(54) **Process for sizing textile materials.**

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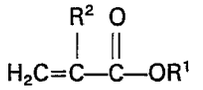
Description

The present invention relates to a process for sizing a textile substrate material by treating the same with a sizing composition comprising an aqueous solution of a copolymer of a acrylamide and at least one polymerizable monomer of, e.g., the formula (I)



(I)

wherein R^1 represents C_1—C_{18} alkyl, or substituted C_1—C_{18} alkyl wherein the substituents are hydroxy, C_1—C_8 alkoxy, C_1—C_8 alkylamino, or di(C_1—C_8 alkyl) amino, and R^2 represents C_1—C_4 alkyl and hydrogen.

By the sizing process of the invention, there are also obtained abrasion-resistant products.

The use of homopolymers of acrylamide as sizing agents for warp yarns, to prevent breaking of the yarn during weaving, is well-known. They perform only slightly better than starch, a commonly employed textile size that imparts only minor protection to fibers during weaving. The moderate performance of polyacrylamide and starch is due to the brittleness of their films on the fiber.

The use of random copolymers of acrylamide and other vinyl or vinylidene comonomers, which comprise from 1 to 40% of said comonomer, as sizes, is known from US—A—3 114 651; GB—A—1 126 120; and DE—A—2 527 804. However, the sizing effect obtainable with the prior art compositions is not sufficient.

The use of a random copolymer of acrylamide and acrylic acid, containing a minor amount of acrylic acid monomer, as a sizing agent, is disclosed by Petrov et al (see Chem. Abstracts 90:105488b). However, these sizes have two components that are both polar and hydrophilic, whereas the sizes of this invention involve at least one hydrophobic and less polar component that can alter the properties of the product such as lubricity, adhesion, and film flexibility.

The present invention provides a process for sizing a textile substrate material comprising applying to the textile material a composition comprising an aqueous solution of at least 3% by weight solids content of a copolymer of acrylamide and at least one hydrophobic vinyl or vinylidene polymerizable monomer, the amount of said polymerizable monomer in the composition being at a concentration of from 1% to about 40%, based on the weight of acrylamide in the composition, characterized in that said copolymer is a segmented copolymer and after application of the composition to the textile material the same is dried at a temperature ranging from 80°C to 120°C for 15—0.25 minutes.

In the preparation of segmented copolymers, structures in the form of grafts or blocks are achieved by the sequential addition of the monomers as the polymerization progresses.

The segmented copolymers of the invention which may be a graft or a block copolymer, or a mixture of both, generally produce more flexible films, especially at low relative humidities, and impart better abrasion resistance to warp yarns than random copolymers, or a mixture of a random copolymer and homopolymers having an identical monomer composition as the segmented copolymer. For example, a blended mixture of a random copolymer of acrylamide and 2-ethylhexyl acrylate, poly(n-butyl acrylate), and polyacrylamide does not perform as well as a segmented copolymer, having an identical monomer composition, in terms of both film flexibility and abrasion resistance.

Other advantages of segmented copolymers are as follows:

1. They impart better yarn-to-yarn and yarn-to-metal abrasion resistance for yarns than starch, or polyacrylamide sizes.

2. They can be applied from more concentrated solutions than starch. This permits an application with less water, thus saving drying time and energy.

3. The pad baths are more easily prepared because of the high solubility of the size in water.

4. The application solutions are stable, and do not retrograde like those containing starch.

5. The polymeric sizing agent is readily removed from the textile substrate by rinsing the cold water.

6. The treated yarns do not have any dry splitting difficulty during slashing.

In preparing the segmented copolymers to be applied in the process of this invention, 30—99% by weight of acrylamide, and about 0—20% by weight of a polymerizable monomer of e.g. formula (I), or mixture of these monomers, is polymerized randomly in an aqueous medium, under an inert atmosphere, in the presence of a surface-active agent and a catalytic amount of a free-radical source, such as ammonium persulfate, ammonium persulfate and sodium bisulfite, and the like. A second charge of 1—20% by weight of a polymerizable monomer, or mixture of monomers, of e.g. formula (I), based on the total weight of polymer, is added from 5 minutes to 5 hours after the addition of the catalyst, and the reaction mixture is stirred for 10—60 minutes. Preferably, the second charge is added at the peak of the ensuing exotherm, after the addition of the catalyst, when very little monomer remains. Optionally, 1—30% by weight of a water-soluble vinylic monomer, such as acrylamide, acrylic acid, or methacrylic acid, based on the total weight of polymer, may be added as a third charge. The reaction mixture is stirred under the inert atmosphere until the copolymerization is essentially completed. The product is a semi-viscous solution that can be applied directly to the textile substrate.

Suitable polymerizable monomers of formula (I) include the following:

methyl acrylate,
ethyl acrylate,
n-butyl acrylate,
2-ethylhexyl acrylate,
2-hydroxyethyl acrylate,
2-methoxyethyl acrylate,
methyl methacrylate,
n-dodecyl methacrylate,
n-octadecyl methacrylate,
N,N-dimethyl-12-aminododecylacrylate,
12-hydroxydodecyl acrylate,
12-methoxydodecyl methacrylate,
N-2-ethylhexyl-2-aminoethyl acrylate,
N-tert-butyl-2-aminoethyl methacrylate,
N,N-dimethyl-2-aminoethyl acrylate,
N,N-diethyl-2-aminoethyl methacrylate,

and the like.

The preferred comonomers are n-butyl acrylate and 2-ethylhexyl acrylate.

Optionally, starch or other sizes may be blended with the product and other conventional additives, such as plasticizers, may be added to the solution before application. Suitable plasticizers include glycerol, ethanolamine, ethylene glycol, polyethylene glycol, urea, sugar, sorbitol, and the like.

In preparing the solution to be applied in the process of this invention, acrylamide and 1—40%, preferably 5—20%, by weight of a hydrophobic polymerizable vinyl, or vinylidene monomer, or mixture of monomers, based on the weight of acrylamide, are copolymerized in an aqueous medium, under an inert atmosphere, in the presence of a surface-active agent and a catalytic amount of a free-radical source such as ammonium persulfate, ammonium persulfate and sodium bisulfite, and the like. The reaction mixture is stirred under the inert atmosphere until the copolymerization is essentially completed. The product is a semi-viscous solution that can be applied directly to the textile substrate. Optionally, starch or other sizes may be blended with the product, the other conventional additives, such as plasticizers, may be added to the solution before application. Suitable plasticizers include glycerol, ethanolamine, ethylene glycol, polyethylene glycol, urea, sugar, sorbitol, and the like.

Suitable vinyl and vinylidene comonomers include the same polymerizable monomers of formula I, listed, above.

The preferred comonomer for the copolymer process is a C_4—C_{18} alkyl acrylate or methacrylate.

The application of the sizing composition to the textile material may be by padding (conventional, or high pressure), foaming, spraying, knife-coating, and the like, to deposit thereon 3—15%, preferably 6—12%, by weight of real solids from the aforementioned reaction mixture. Suitable textile materials include filaments, spun yarns, or fabrics of natural or syntheric fibers, or blends thereof. The preferred substrate material is cotton, or cotton/polyester warp yarn.

The treated textile substrate is then dried by heating at 80—120°C for a period of 15 to 0.25 minutes, preferably at 95—105°C for a period of 2 to 0.5 minutes.

The process of this invention produces a size coating on the textile substrate which is characterized by easy removal by subsequent washing. The treated textile substrate is characterized by excellent abrasion resistance.

The following examples illustrate the process of preparation of the segmented copolymer of the invention. All parts and percentages are by weight unless otherwise indicated.

Example 1

A mixture of 152 grams of an aqueous solution of acrylamide (50% real solids), 4.0 grams of 2-ethyl-hexyl acrylate, 1.0 gram of AEROSOL® OT-75% (American Cyanamid Company), and 272 grams of water is stirred under nitrogen for 20 minutes at 30—35°C. Solutions of 0.4 gram of ammonium persulfate in 5 grams of water, and 0.4 gram of sodium metabisulfite in 5 grams of water are added thereto and the temperature is allowed to rise spontaneously. At the peak of the resulting exotherm, 10 grams of 2-ethylhexyl acrylate is added. The reaction mixture is stirred for one hour, and then cooled to 25°C to obtain a solution having a viscosity of 340 mPa.s and a polymer content of 20% by weight.

Example 2

A mixture of 174.7 grams of an aqueous solution of acrylamide (50% real solids), 3.5 grams of 2-ethylhexyl acrylate, 1.2 grams of AEROSOL® OT-75%, and 194 grams of water is stirred under nitrogen for 20 minutes at 30—35°C. Solutions of 0.5 gram of ammonium persulfate in 6 grams of water, and 0.5 gram of sodium metabilsulfite in 6 grams of water are added thereto and the temperature is allowed to rise spontaneously. At the peak of the exotherm, 9.2 grams of *n*-butyl acrylate is added. The reaction mixture is

stirred for one and a half hours, then cooled to 25°C to obtain a solution having a viscosity of 600 mPa.s, and a polymer content of 25% by weight.

Example 3

A mixture of 152 grams of an aqueous solution of acrylamide (50% real solids), 4.0 grams of 2-ethylhexyl acrylate, 1.0 grams of AEROSOL® OT-75%, and 332 grams of water is stirred under nitrogen for 20 minutes at 30—35°C. Solutions of 0.4 gram of ammonium persulfate in 5 grams of water, and 0.4 gram of sodium metabisulfite in 5 grams of water are added thereto and the temperature is allowed to rise spontaneously. At the peak of the exotherm, 10 grams of styrene is added. The mixture is stirred for 30 minutes, and 40 grams of 50% aqueous acrylamide is then added thereto. After one hour of continued stirring, the reaction mixture is cooled to 25°C to obtain a solution having a viscosity of 400 mPa.s and a polymer content of 20% by weight.

Example 4

A mixture of 152 grams of an aqueous solution of acrylamide (50% real solids), 4.0 grams of 2-ethylhexyl acrylate, 1.0 gram of AEROSOL® OT-75%, and 260 grams of water is stirred under nitrogen for 20 minutes at 30—35°C. Solutions of 0.4 gram of ammonium persulfate in 5 grams of water, and 0.4 gram of sodium metabisulfite in 5 grams of water are added thereto, and the temperature is allowed to rise spontaneously. At the peak of the exotherm, 10 grams of *n*-butyl acrylate is added. The reaction mixture is stirred for 30 minutes, and 10 grams of acrylic acid is then added to the reaction mixture. After one hour of continued stirring, the reaction mixture is cooled to 25°C to obtain a solution having a viscosity of 220 mPa.s and a polymer content of 20% by weight.

Example 5

A mixture of 2165 grams of an aqueous solution of acrylamide (50% real solids), 32.7 grams of 2-ethylhexyl acrylate, 8.2 grams of AEROSOL® OT-75%, and 500 grams of water is stirred under nitrogen for 20 minutes at 20—25°C. Solutions of 2.9 grams of ammonium persulfate in 43 grams of water, and 2.9 grams of sodium metabisulfite in 43 grams of water are added thereto, and the temperature is allowed to rise spontaneously. At the peak of the exotherm, 81.8 grams of *n*-butyl acrylate is added. The reaction mixture is stirred for 20 minutes, and 327 grams of 50% aqueous acrylamide is then added. After one hour of continued stirring, the reaction mixture is cooled to 25°C to obtain a solution having a viscosity of 720 mPa.s and a polymer content of 20% by weight.

Example 6

A mixture of 152 grams of an aqueous solution of acrylamide (50% real solids), 4.0 grams of *n*-butyl acrylate, 1.0 grams of AEROSOL® OT-75%, and 332 grams of water is stirred under nitrogen for 20 minutes at 30—35°C. Solutions of 0.6 gram of ammonium persulfate in 5 grams of water, and 0.6 gram of sodium metabisulfite in 5 grams of water are added thereto and the temperature is allowed to rise spontaneously. At the peak of the exotherm, 10 grams of *n*-butyl acrylate is added. The reaction mixture is stirred for 20 minutes, and 40 grams of 50% aqueous acrylamide is then added. After one hour of continued stirring, the reaction mixture is cooled to 25°C to obtain a solution having a viscosity of 720 mPa.s, and a polymer content of 20% by weight.

Examples 7—12

The solutions from Examples 1—6 are diluted with water to obtain a polymer content of 10% by weight and applied separately, by padding, to single-end 100% cotton yarns to obtain a 60% pickup based on the weight of the untreated yarn. The treated yarns are dried at 105°C for one minute and tested for abrasion resistance using a modified Stoll flex abrader. In this test five strands of the treated yarns are attached to a Stoll flex abrader so that all are flexed over a stainless steel blade at a 90° angle using an attached 20-gram weight as a pulling force. The motor is started and the number of cycles needed to break each yarn is determined. This procedure is repeated three times for similarly treated yarns and an average is taken. The larger the number of cycles, the better the abrasion resistance imparted to the yarn.

The results obtained are shown in Table I.

TABLE 1

Example	Sizing agent	Average abrasion resistance (cycles)
7	Product of Example 1	149
8	Product of Example 2	200
9	Product of Example 3	152
10	Product of Example 4	165
11	Product of Example 5	216
12	Product of Example 6	215
	Untreated cotton yarn	62

Comparative examples 13—15

Solutions containing 10% by weight, respectively, of starch; a random terpolymer of acrylamide, n-butyl acrylate, and 2-ethylhexyl acrylate having the same monomer composition as in Example 5; and a blended mixture of a copolymer of acrylamide and 2-ethylhexyl acrylate, poly(n-butyl acrylate), and poly(acrylamide) having the same monomer composition as in Example 5, are prepared and applied to single-end 100% cotton yarns as described in Examples 7—12.

The results obtained are shown in Table II.

TABLE II

Example	Sizing agent	Average abrasion resistance (cycles)
13	Starch	92
14	Terpolymer	156
15	Blended mixture	176
	Untreated cotton yarn	62

Comparison of the results obtained in Examples 14 and 15 with that obtained in Example 11 shows that superior abrasion resistance is obtained with the segmented copolymer of Example 5.

Claims

1. A process for sizing a textile substrate material comprising applying to the textile material a composition comprising an aqueous solution of at least 3% by weight solids content of a copolymer of acrylamide and at least one hydrophobic vinyl or vinylidene polymerizable monomer, the amount of said polymerizable monomer in the composition being at a concentration of from 1% to 40%, based on the weight of acrylamide in the composition, characterized in that said copolymer is a segmented copolymer and after application of the composition to the textile material the same is dried at a temperature ranging from 80°C to 120°C for 15—0.25 minutes.

2. The process according to Claim 1 wherein the composition comprises a solution in water of a segmented copolymer of Claim 1 at a concentration from 5% to 30% by weight of the segmented copolymer, based on the weight of the composition, the composition being applied to the textile material to deposit the copolymer in an amount from 3% to 15% by weight, based on the weight of the material, and said textile material is dried at a temperature ranging from 80°C to 120°C for 15—0.25 minutes.

3. The process according to Claim 2 wherein the amount of segmented copolymer deposited on the textile material is from 6% to 12% by weight, based on the weight of the material, and said textile material is dried at a temperature from 95°C to 105°C for 2—0.5 minutes.

4. The process according to Claim 1 wherein the textile material is a cotton yarn, cotton/polyester yarn or polyester yarn.

5. The process according to Claim 2 wherein the hydrophobic vinyl polymerizable monomer is a C_4—C_{18} alkyl acrylate, or a C_4—C_{18} alkyl methacrylate.

6. The process according to Claim 5 wherein the C_4—C_{18} alkyl acrylate is a mixture of 2-ethylhexyl acrylate and n-butyl acrylate.

7. The process according to Claim 6 wherein the C_4—C_{18} alkyl acrylate is n-butyl acrylate.

8. A sized textile material obtainable by the process of claim 4.

9. A textile sizing composition comprising an aqueous solution of at least 3% by weight solids content of a copolymer of acrylamide and at least one hydrophobic vinyl, or vinylidene, polymerizable monomer, the amount of said polymerizable monomer in the composition being at a concentration from 1% to 40%, based on the weight of acrylamide in the composition, characterized in that said copolymer is a segmented copolymer.

Patentansprüche

1. Verfahren zum Schlichten eines Textilsubstratmaterials, wobei man auf das Textilmaterial ein Mittel appliziert, welches eine wässrige Lösung von mindestens 3 Gew.-% Feststoffgehalt eines Copolymeren von Acrylamid und mindestens einem hydrophoben Vinyl- oder Vinyliden-polymerisierbaren Monomeren umfaßt, wobei die Menge des polymerisierbaren Monomeren in dem Mittel bei einer Konzentration von 1 bis 40 Gew.-%, bezogen auf das Gewicht von Acrylamid in dem Mittel, beträgt, dadurch gekennzeichnet, daß das Copolymere ein segmentiertes Copolymeres ist und daß das Textilmaterial nach Applikation des Mittels bei einer Temperatur im Bereich von 80 bis 120°C während 15 bis 0,25 Minuten getrocknet wird.

2. Verfahren gemäß Anspruch 1, wobei das Mittel eine Lösung eines segmentierten Copolymeren gemäß Anspruch 1 in Wasser in einer Konzentration von 5 bis 30 Gew.-% des segmentierten Copolymeren, bezogen auf das Gewicht des Mittels, umfaßt, das Mittel auf das Textilmaterial appliziert wird, um das Copolymere in einer Menge von 3 bis 15 Gew.-%, bezogen auf das Gewicht des Materials, zu applizieren und das Textilmaterial bei einer Temperatur im Bereich von 80 bis 120°C während 15 bis 0,25 Minuten getrocknet wird.

3. Verfahren gemäß Anspruch 2, wobei die Menge des segmentierten Copolymeren, das auf dem Textilmaterial abgeschieden wird, von 6 bis 12 Gew.-%, bezogen auf das Gewicht des Materials, beträgt und das Textilmaterial bei einer Temperatur von 95 bis 105°C während 2 bis 0,5 Minuten getrocknet wird.

4. Verfahren gemäß Anspruch 1, wobei das Textilmaterial Baumwollgarn, Baumwollpolyestergarn oder Polyestergarn ist.

5. Verfahren gemäß Anspruch 2, wobei das hydrophobe Vinyl-polymerisierbare Monomere ein C_4—C_{18}-Alkylacrylat oder ein C_4—C_{18}-Alkylmethacrylat ist.

6. Verfahren gemäß Anspruch 5, wobei das C_4—C_{18}-Alkylacrylat ein Gemisch von 2-Ethylhexylacrylat und n-Butylacrylat ist.

7. Verfahren gemäß Anspruch 6, wobei das C_4—C_{18}-Alkylacrylat n-Butylacrylat ist.

8. Geschlichtetes Textilmaterial, erhältlich nach dem Verfahren von Anspruch 4.

9. Textil-Schlichtmittel, umfassend eine wässrige Lösung von mindestens 3 Gew.-% Feststoffgehalt eines Copolymeren von Acrylamid und mindestens einem hydrophoben Vinyl- oder Vinyliden-polymerisierbaren Monomeren, wobei die Menge des polymerisierbaren Monomeren in dem Mittel von 1 bis 40%, bezogen auf das Gewicht von Acrylamid in dem Mittel, beträgt, dadurch gekennzeichnet, daß das Copolymere ein segmentiertes Copolymeres ist.

Revendications

1. Procédé d'encollage d'un matériau formant substrat textile, dans lequel on applique sur le matériau textile une composition comprenant une solution aqueuse ayant une teneur en solides d'au moins 3% en poids d'un copolymère d'acrylamide et d'au moins un monomère hydrophobe polymérisable de vinyle ou de vinylidène, la quantité dudit monomère polymérisable dans la composition correspondant à une concentration de 1% à 40% par rapport au poids d'acrylamide dans la composition, caractérisé en ce que ledit copolymère est un copolymère segmenté et en ce qu'après l'application de la composition sur le matériau textile, ce dernier est séché à une température allant de 80°C à 120°C pendant 15 à 0,25 minutes.

2. Procédé suivant la revendication 1, dans lequel la composition comprend une solution dans l'eau d'un copolymère segmenté suivant la revendication 1 à une concentration de 5% à 30% en poids du copolymère segmenté par rapport au poids de la composition, la composition étant appliquée sur le matériau textile pour déposer le copolymère en une quantité de 3% à 15% en poids par rapport au poids du matériau, et dans lequel ledit matériau textile est séché à une température allant de 80°C à 120°C pendant 15 à 0,25 minutes.

3. Procédé suivant la revendication 2, dans lequel la quantité de copolymère segmenté déposée sur le matériau textile est de 6% à 12% en poids par rapport au poids du matériau, et dans lequel ledit matériau textile est séché à une température de 95°C à 105°C pendant 2 à 0,5 minutes.

4. Procédé suivant la revendication 1, dans lequel le matériau textile est un fil en coton, un fil en coton/polyester ou un fil en polyester.

5. Procédé suivant la revendication 2, dans lequel le monomère hydrophobe polymérisable de vinyle, est un acrylate d'alkyle en C_4—C_{18} ou un méthacrylate d'alkyle en C_4—C_{18}.

6. Procédé suivant la revendication 5, dans lequel l'acrylate d'alkyle en C_4—C_{18} est un mélange d'acrylate de 2-éthylhexyl et d'acrylate de n-butyle.

7. Procédé suivant la revendication 6, dans lequel l'acrylate d'alkyle en C_4—C_{18} est de l'acrylate de n-butyle.

8. Matériau textile encollé obtenu suivant le procédé de la revendication 4.

9. Composition d'encollage de textile, comprenant une solution aqueuse d'une teneur en solides d'au moins 3% en poids d'un copolymère d'acrylamide et d'au moins un monomère hydrophobe polymérisable de vinyle ou de vinylidène, la quantité dudit monomère polymérisable dans la composition correspondant à une concentration de 1% à 40% par rapport au poids d'acrylamide dans la composition, caractérisée en ce que ledit copolymère est un copolymère segmenté.