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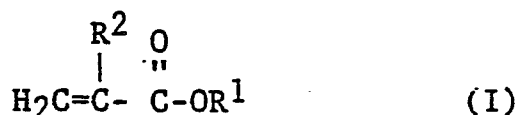
(54) Process for sizing textile materials.

(57) This invention relates to a process for sizing textile yarns by treatment with copolymers, and/or multi-polymers, of acrylamide, and to the products thereby obtained.

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In accordance with the invention, there is provided a process for sizing textile yarns by treatment of the same with copolymers, segmented copolymers, and/or multipolymers, of acrylamide, and at least one polymerizable monomer of formula (I)



wherein  $\text{R}^1$  represents hydrogen,  $\text{C}_1$ - $\text{C}_{18}$  alkyl, or substituted  $\text{C}_1$ - $\text{C}_{18}$  alkyl wherein the substituents are hydroxy,  $\text{C}_1$ - $\text{C}_8$  alkoxy,  $\text{C}_1$ - $\text{C}_8$  alkylamino, or di( $\text{C}_1$ - $\text{C}_8$  alkyl)amino, and  $\text{R}^2$  represents  $\text{C}_1$ - $\text{C}_4$  alkyl and hydrogen.

In accordance with the invention, there are also obtained abrasion-resistant products obtained by the sizing process of the invention.

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.

Although random copolymers of acrylamide and other vinyl, or vinylidene monomers have also been used as sizes for warp yarns, almost invariably the acrylamide they contain is a minor component of the copolymer. Consequently, such sizes are, therefore, often water-insoluble and difficult to desize.

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  
5 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.

10 In the preparation of random copolymers of acrylamide, acrylamide and the comonomer, or comonomers, are well-mixed in a reaction vessel before initiating polymerization.

In the preparation of segmented copolymers,  
15 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  
20 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.  
25 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  
30 resistance.

Other advantages of segmented copolymers are as follows:

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1. They impart better yarn-to-yarn and yarn-to-metal abrasion resistance for yarns than starch, or polyacrylamide sizes.
- 5 2. They can be applied from more concentrated solutions than starch. This permits an application with less water, thus saving drying time and energy.
- 10 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.
- 15 5. The polymeric sizing agent is readily removed from the textile substrate by rinsing with cold water.
- 20 6. The treated yarns do not have any dry splitting difficulty during slashing.

In preparing the composition to be applied in the segmented copolymer process of this invention, 30-99% by weight of acrylamide, and about 0-20% by weight of a polymerizable monomer of 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 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

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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  
5 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)  
10 include the following:

methyl acrylate,  
ethyl acrylate,  
n-butyl acrylate,  
2-ethylhexyl acrylate,  
15 2-hydroxyethyl acrylate,  
2-methoxyethyl acrylate,  
methyl methacrylate,  
n-dodecyl methacrylate,  
n-octadecyl methacrylate,  
20 N,N-dimethyl-12-aminododecylacrylate,  
12-hydroxydodecyl acrylate,  
12-methoxydodecyl methacrylate,  
acrylic acid,  
methacrylic acid,  
25 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.

30 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  
35 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 copolymer process of this invention, acrylamide and about 1-40%, preferably about 5-20%, by weight of a 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, 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.

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<sub>4</sub>-C<sub>18</sub> 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 about 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 synthetic 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 about 15 to 0.25 minutes, preferably at 95-105°C for a period of about 2 to 0.5 minutes. Optionally, the treated substrate may be

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dried at a lower temperature, such as by standing at room temperature until dry.

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 the segmented copolymer 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-ethylhexyl 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 centipoises, 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 metabisulfite 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 centipoises, and a polymer

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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-ethyl-  
5 hexyl 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  
10 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  
15 25°C to obtain a solution having a viscosity of 400 centipoises 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-ethyl-  
20 hexyl 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 tempera-  
25 ture 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  
30 mixture is cooled to 25°C to obtain a solution having a viscosity of 220 centipoises and a polymer content of 20% by weight.

#### Example 5

A mixture of 2165 grams of an aqueous solution  
35 of acrylamide (50% real solids), 32.7 grams of 2-ethyl-hexyl acrylate, 8.2 grams of AEROSOL® OT-75%, and 500 grams of water is stirred under nitrogen for 20 minutes



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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 centipoises, 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 gram 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 centipoises, 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

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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  
5 number of cycles, the better the abrasion resistance imparted to the yarn.

The results obtained are shown in Table I.

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TABLE I

<u>Example</u>	<u>Sizing Agent</u>	<u>Average Abrasion Resistance (cycles)</u>
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

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.

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TABLE II

<u>Example</u>	<u>Sizing Agent</u>	<u>Average Abrasion Resistance (cycles)</u>
13	Starch	92
14	Terpolymer	156
15	Blended mixture	176
	Untreated cotton yarn	62

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

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

Example 16

5           A mixture of 30.9 grams of acrylamide (97% real), 3.0 grams of n-butyl acrylate, 0.3 gram of ammonium persulfate, 1.5 grams of a nonionic surfactant (DECERESOL® Surfactant NI Conc.; American Cyanamid Co.), and 3.0 grams of isopropanol, is blended under nitrogen, and diluted  
10   with water to a total weight of 330 grams. The diluted mixture is heated to 70°C to initiate polymerization. The heating is discontinued when the temperature reaches 85°C. The mixture is then stirred at 35-40°C for 2 hours and cooled to room temperature. The final solution has  
15   a viscosity of 1875 centipoises.

Example 17

          A mixture of 240 grams of an aqueous solution of acrylamide (50% real solids), 6.0 grams of 2-ethylhexyl acrylate, 0.3 gram of ammonium persulfate, 2.0  
20   grams of DECERESOL® Surfactant NI Conc., 6.0 grams of isopropanol, and 473.7 grams of water is mixed under nitrogen, and heated to 70°C. The temperature is allowed to rise to 92°C. and then maintained at 85-90°C for one hour while stirring the reaction mixture. The mixture  
25   is then cooled to room temperature to obtain a solution having a viscosity of 640 centipoises.

Example 18

          A mixture of 240 grams of acrylamide (50% real), 6.0 grams of 2-ethylhexyl acrylate, 6.0 grams of methyl  
30   methacrylate, 0.3 gram of ammonium persulfate, 2.0 grams of DECERESOL Surfactant NI Conc., 4.0 grams of isopropanol, and 527.7 grams of water is mixed under nitrogen, and heated to 70°C. The temperature is allowed to rise to 93°C and then maintained at 87-93°C for 2 hours while  
35   stirring the reaction mixture. The mixture is then cooled to room temperature to obtain a solution having a viscosity of 600 centipoises.

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Example 19

A mixture of 152 grams of an aqueous solution of acrylamide (50% real solids), 4.0 grams of 2-ethylhexyl acrylate, 1.5 grams of AEROSOL® OT-75%, and 232.4 grams of water is stirred under nitrogen for 20 minutes at ambient temperature. Solutions of 0.3 gram of ammonium persulfate in 5 grams of water, and 0.3 gram of sodium bisulfite in 5 grams of water are added thereto and the temperature is allowed to rise spontaneously. The reaction mixture is stirred for one hour, then cooled to 25°C to obtain a solution having a viscosity of 540 centipoises.

Example 20

A mixture of 1.5 grams of AEROSOL® OT-75% and 237.3 grams of water is heated to dissolve the surfactant, then cooled to room temperature. The solution is stirred under nitrogen and 120 grams of an aqueous solution of acrylamide (50% real solids), 4.0 grams of 2-ethylhexyl acrylate, and 16.2 grams of acrylic acid are added thereto. Solutions of 0.5 gram of ammonium persulfate in 10 grams of water, and 0.5 gram of sodium metabisulfite in 10 grams of water, are added thereto while allowing the temperature to rise. After stirring for 1.5 hours, the reaction mixture is cooled to room temperature to obtain a solution having a viscosity of 620 centipoises, and a pH of 2.5. Before application the pH of the material is adjusted to 5-7 with sodium hydroxide.

Examples 21-27

The solutions from Examples 16-20 are diluted with water to obtain a solids content of 7.5% by weight and applied separately, by padding, to single-end 100% cotton yarns to obtain an 80% wet pickup based on the weight of the untreated yarn. Solutions containing 7.5% by weight of polyacrylamide in water, and starch in water, are also prepared and applied to single-end 100% cotton yarns in a similar manner. The treated yarns are dried at 105°C for one minute and tested for abrasion



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resistance using a modified Stoll flex abrader. In this test five strands of the treated yarns are attached to a Stoll flex brader so that all are flexed over a stainless steel blade at 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 average, the better the abrasion resistance imparted to the yard.

The results obtained are shown in Table III.

TABLE III

		Average Abrasion	
<u>Example</u>		<u>Sizing Agent</u>	<u>Resistance (cycles)</u>
15	21	Product of Example 16	105
	22	Product of Example 17	119
	23	Product of Example 18	113
	24	Product of Example 19	113
	25	Product of Example 20	106
20	26	Polyacrylamide	89
	27	Starch	92
		Untreated cotton yarn	62

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## I Claim:

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 or a segmented copolymer of acrylamide and at least one vinyl, or vinylidene, polymerizable monomer, the amount of the polymerizable monomer in the composition being at a concentration from about 1% to about 40%, based on the weight of acrylamide in the composition, and thereafter drying the treated substrate, the composition being applied in an amount and the drying being at a temperature, respectively, sufficiently high to impart a high order of abrasion resistance to the textile material.

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 about 5% to about 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 about 3% to about 15% by weight, based on the weight of the material, and drying the same at a temperature ranging from about 80°C to about 120°C for about 15-0.25 minutes.

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

4. The process according to Claim 2 wherein the amount of segmented copolymer deposited on the textile material is from about 6% to about 12% by weight;

based on the weight of the material, and drying the same at a temperature from about 95°C to about 105°C for about 2-0.5 minutes.

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

6. The process according to Claim 2 wherein the vinyl polymerizable monomer is a C<sub>4</sub>-C<sub>18</sub> alkyl acrylate, or a C<sub>4</sub>-C<sub>18</sub> alkyl methacrylate.

7. The process according to Claim 6 wherein the C<sub>4</sub>-C<sub>18</sub> alkyl acrylate is a mixture of 2-ethylhexyl acrylate and n-butyl acrylate.

8. The process according to Claim 7 wherein the C<sub>4</sub>-C<sub>18</sub> alkyl acrylate is n-butyl acrylate.

9. The treated textile material of Claim 5.

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