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3,455,735

PROCESS FOR RENDERING A SYNTHETIC POLYMERIC TEXTILE MATERIAL ANTISTATIC AND THE RESULTING MATERIAL

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No Drawing. Filed May 12, 1966, Ser. No. 549,490

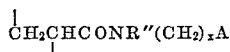
Int. Cl. D06m 13/40; B44d 1/22

U.S. Cl. 117—138.8

3 Claims

ABSTRACT OF THE DISCLOSURE

A textile substrate consisting essentially of a polyester polymer and having a durable antistatic coating of a polyamide, said polyamide consisting essentially of repeating structural units of the formula



in which R'' is selected from the group consisting of hydrogen, lower alkyl containing 1 to 4 carbon atoms and (CH₂)_xA, x is an integer from 2 to 3, and A is selected from the group consisting of —OH and —CN, said coating being present in an antistatic amount up to about 5% by weight of the substrate. Also disclosed is a process for making the antistatic polyester textile which comprises applying to the substrate an aqueous solution of a member selected from the group consisting of cyanoethyl and hydroxyethyl amine salts of polyacrylic acid, drying the treated substrate, and then heating the treated substrate at an elevated temperature until the amine salt is substantially all converted to the corresponding amide.

This invention relates to synthetic polymer filaments and fibers which will not accumulate a charge of static electricity as a result of friction. More particularly it is concerned with synthetic polymer filaments and fibers which are antistatic due to surface coatings composed of polyamides derived from unsaturated polymerizable acids and cyanoalkyl or hydroxyalkyl amines.

The development of static in synthetic textile fibers and fabrics composed therefrom is a well recognized problem. Despite the availability of a large number of antistatic materials, most are lacking in one or more of the requirements for an antistatic coating. For example, most are not sufficient durable to washing or drycleaning, or they discolor or stiffen the fibers, or are neutralized by drycleaning soaps or have other deficiencies.

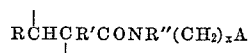
The present discovery provides antistatic coatings for synthetic textile fibers and textile products made therefrom which coatings are durable to laundering and drycleaning and are not sensitive to drycleaning soaps. Furthermore, these coatings do not appreciably discolor nor stiffen the fibers.

These results are obtained in accordance with the present invention by applying to synthetic textile fibers a coating composition of a polyamide of a polymerizable acid and a cyanoalkyl or hydroxyalkyl amine. The textile substrate can be treated with a solvent solution or with

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an aqueous dispersion of the polyamide or the polyamide can be formed in situ on the fiber by applying the amine salt of the polyacid and then heating the treated fiber to convert the salt to the amide.

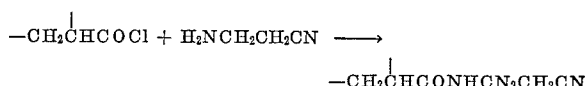
For the purposes of this invention the polyamides are provided having the repeating structural unit



where R and R' are hydrogen or lower alkyl of 1 to 4 carbons, R'' is hydrogen, alkyl of 1 to 4 carbons or (CH₂)_xA, x is an integer from 2 to 4, and A is —OH or —CN.

The polyamide coatings normally are above 10,000 molecular weight and can range upwardly of 200,000 or 300,000 or even more. It has been noted that the higher molecular weight polyamides provide antistatic coatings of greater durability compared with that achieved with the very low molecular weight materials. Based on the weight of the textile substrate to which it is applied, at least 0.25 weight percent, and suitably about 0.4 to 5 weight percent of coating is applied.

Particularly suitable compositions of this invention are the amides of polymerized acrylic, methacrylic or crotonic acids with hydroxyethyl amine or cyanoethyl amine. These polyamides can be prepared by reacting polyacryloyl chloride with the appropriate amine as follows:



The dicyanoethyl derivative can be made likewise from 3,3'-imino-dipropionitrile. This latter compound is easily prepared by reacting acrylonitrile with ammonium hydroxide in aqueous solution. It is also possible to partially cyanoethylate acrylamide with acrylonitrile but the resulting products are less laundry-resistant. The hydroxyethyl amides are made in the same way by reacting the polyacid chloride with ethanolamine or diethanolamine.

The poly-cyanoethyl amides or -hydroxyethyl amides can be applied to the textile substrate from solution in an organic solvent or from an aqueous dispersion or as an aqueous emulsion of an organic solution thereof. The cyanoethyl acrylamides are soluble in dimethyl formamide or acetonitrile and can be applied to polyester and polyamide fibers or fabrics from these solvents. The hydroxyethyl acrylamides are soluble in lower alcohols and in ketones such as methanol and acetone, respectively.

The most practical method of applying a coating of the present invention is to treat the fiber or fabric with the cyanoethyl or hydroxyethyl amine salt of the polyacid and convert the salt to the amide in situ. This conversion is readily accomplished by heating the treated substrate at an elevated temperature, for example about 140° to 190° C., for a few minutes, i.e. ½ to 8 minutes or so. The time and temperature of the heat treatment should be controlled to avoid embrittlement of the coating, which can result in loss of a substantial part of the antistatic activity. By way of example, in applying hydroxyethyl amine salt and heating, the resulting coating contains about 90 percent of amide and about 10 percent of ester, based on estimates from infrared spectrums.

The method of applying the water-soluble amine salt

of a polyacrylic acid and a cyanoethyl amine or a hydroxyethyl amine allows the convenient use of more than a

out detergent. It is then freed of solvent by centrifuging and air drying.

TABLE I

Number of dry cleanings	Fabric load percent treated	Charge decay (seconds)					
		Log R		T 1/2		T-500	
		Treated	Untreated	Treated	Untreated	Treated	Untreated
0-----	0.93	12.5	15.0	1	110	1	>300
1-----	0.91	12.8	15.0	2	105	6	>300
6-----	1.77	12.2	15.0	3	105	1/2	>300

single amine in a polymer, or mixtures of cyanoalkyl amines and hydroxyalkyl amines can be used. It is also possible to cross-link the amides further after they are formed and thus improve the wash-fastness of the resulting finish, although this will usually decrease the antistatic effect somewhat. Cross-linking can be accomplished by the use of certain bifunctional compounds such as carbonylhydrazide, or other dihydrazides, or by heating the dicyanoethyl or dihydroxyethyl acrylamides themselves.

The invention will be described further in conjunction with the following specific examples.

Example I

About 70 grams of freshly distilled acrylic acid is added to 900 ml. of distilled water in a container. Then additional distilled water is added to bring the volume to 1000 ml. Potassium persulfate, in an amount of 0.25 gram, is added to the solution, and the solution is then heated to 80° to 85° C. on a steam bath, while a stream of nitrogen is constantly bubbled through the solution by means of a glass tube immersed therein. After 10 minutes the solution becomes viscous; after 15 minutes of polymerization, the reaction is stopped by adding 0.5 gram of hydroquinone dissolved in 3 ml. of water. The room temperature viscosity of the solution is found to be 14 centipoises, corresponding to a molecular weight of about 80,000.

Polyacrylic acid for the following examples is made as just described. This acid is nearly identical to a commercially available polyacrylic acid, Acrysol A-3, which has similar viscosity and molecular weight, and which could as well be used.

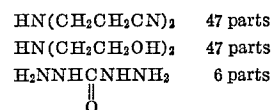
Example II

A 5% aqueous solution of polyacrylic acid, made by the procedure of Example I, is neutralized with monoethanol amine to a pH of approximately 8.0 and the solution is diluted with water to give 2% of the amine salt in solution. This solution is used to impregnate a fabric of taffeta design woven from polyester yarns. The excess solution is squeezed out and the fabric is air dried and then heated to 165° C. for 1 min. The fabric is then submitted to drycleaning tests and electrostatic tests to determine the effect of drycleaning. The conductivity of the fabric is determined by the Standard Test Method 76-1964 of the AATCC and is expressed as the logarithm of the resistivity (Log R). The decay time for an electrical charge is measured by first charging the fabric to 500 volts with DC current, if possible, and noting the time for the charge to leak down to 2500 (1/2 T) and to 500 volts. The data obtained are shown in Table I.

The results of Table I show that this treatment makes the fiber antistatic since the charged fabric loses its charge rapidly. The effect is improved after several drycleanings. The drycleanings are carried out as follows: Twenty-five grams of fabric are tumbled for 25 minutes in 750 ml. of chlorinated solvent containing 3.5% mahogany sulfonate detergent and 0.03% water. It is removed from this solution and tumbled for 5 minutes in clean solvent with-

Example III

Aqueous polyacrylic acid is neutralized to pH 7 with a mixture of the following compounds in the proportions shown:



The resulting solution is diluted to a solids concentration of 2% and padded onto polyester taffeta fabric and air dried. Different samples are heated at various temperatures and for various times as recorded, along with the antistatic data, in Table II.

Although the Log R values appear high for antistatic fabrics, the charge decay for these treated fabrics is found to be almost instantaneous and, furthermore, it is found impossible to charge the fabrics to 5000 v. which is standard for the charge decay test. The highest charge which can be obtained on these samples is about 3000 volts. Results in Table II show that the antistatic coating is fast to washing.

TABLE II

Heating,/ temperature/ time, ° C. minutes	Load on fabric		Log R	
	Initial, percent	After 5 laundings, percent	Treated	Untreated
150/3-----	2.16	0.45	14.6	15.0
150/6-----	1.78	1.08	14.2	14.9
150/6-----	1.07	0.67	14.6	-----
150/9-----	1.85	1.43	14.5	15.0
150/9-----	0.71	0.69	14.4	-----
175/1-----	1.78	0.39	14.6	15.0
175/2-----	2.32	1.95	14.5	14.9
175/2-----	1.05	0.80	14.4	-----
175/5-----	1.62	1.66	14.4	14.9
175/5-----	0.69	0.84	14.7	-----

Example IV

A more practical test of antistatic evaluation was devised which will be referred to as the "sail test." In this test the subject, wearing a slip made from treated fabric, rubber soled shoes and nylon stockings, but no dress, walks 6 feet with the slip in contact with a full width of untreated polyester or nylon fabric mounted in a vertical position between two upright posts. By use of a stopwatch the duration of clinging by the slip is noted. The test lasts 10 minutes after the charging but it has been noted that slips of untreated nylon or polyester fibers will continue to cling for over 20 minutes. The static is rated by an arbitrary scale as follows: 5.0 no static; 4.0 slight static; 3.0 moderate static; 2.0 high static; 1.0 severe static.

Table III shows the results of various heating schedules on the static resistance of coated polyester fabrics worn against nylon sails and against polyester sails. Comparison with untreated fabric (test No. 12) shows the effectiveness of the antistatic finishes. In the tabulated tests, the coating solutions for tests 1 and 2 are obtained by reacting polyacrylic acid with a mixture of equal parts of $\text{HN}(\text{CH}_2\text{CH}_2\text{CN})_2$ and $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$; for tests 3 to 7, the solution is as produced in Example III; for tests 8 to 10, the acid is reacted with a mixture of 94 parts of $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$ and 6 parts of carbazide; and for test

11, the acid is reacted with aminopropanol. In each instance, the solution had a pH of about 7. The data obtained are:

A's in any single unit of the polyamide being the same, said coating being present in an antistatic amount up to about 5% by weight of the substrate.

TABLE III

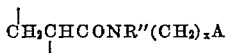
Average sail tests (minutes)											
Test No.	Percent load on fabric	Heated, ° C./min.	Nylon Sail				Polyester Sail				
			Init. static rating	Time to unobj. static	Time to no static	Static after 10 min.	Init. static	Time to unobj. static	Time to no static	Static after 10 min.	
1.-----	1.75	150/4	4.5	.13	.36	5.0	2.5	2.0	6.00	5.0	
2.-----	1.98	175/2	4.2	.50	3-10	4.5	2.3	3.9	6.15	5.0	
3.-----	1.56	150/4	4.7	.06	.13	5.0	2.0	.85	2.90	5.0	
4.-----	1.77	175/2	5.0	.90	.00	5.0	2.3	1.21	2.75	5.0	
5.-----	3.62	150/4	4.5	.43	.80	5.0	3.0	1.50	5.20	5.0	
6.-----	2.48	175/2	4.7	.16	.23	5.0	2.3	2.66	6.5-10+	4.8	
7.-----	2.94	174/4	4.3	.06	.33	5.0	2.0	3.23	10+	4.7	
8.-----	1.86	175/4									
9.-----	3.40	175/2	4.2	.50	.95	5.0	2.0	3.21	4.8-10+	4.8	
10.-----	4.65	175/4	4.5	.00	.00	5.0	2.2	2.40	5.43	5.0	
11.-----	2.62	175/2	3.7	1.01	4.1-10+	4.7	3.0	1.55	4.25	5.0	
12.-----	0		1.0	10+	10+	1.0	1.0	10+	10+	1.0	

Antistatic coatings in accordance with the present discoveries are imparted to textile substrates of continuous or discontinuous filaments. These improvements are particularly significant with filaments of synthetic linear condensation polymers such as the polyamides or polyesters, for example 6-6 nylon and poly(ethylene terephthalate). Polyacrylonitrile can likewise be treated to provide antistatic protection. The coating can be applied to the fibers or filaments in the form of a tow, staple or yarn, or to woven, knit or non-woven fabrics.

While the invention has been described with specific embodiments, it will be evident that changes can be made without departing from its scope.

What is claimed is:

1. A textile substrate consisting essentially of a polyester polymer and having a durable antistatic coating of a polyamide, said polyamide consisting essentially of repeating structural units of the formula



in which R'' is selected from the group consisting of hydrogen, lower alkyl containing 1 to 4 carbon atoms and (CH₂)_xA, x is an integer from 2 to 3, and A is selected from the group consisting of —OH and —CN with the

2. A process for imparting antistatic protection to synthetic textile material consisting essentially of a polyester substrate that is subject to the accumulation of static electricity which comprises applying to the substrate an aqueous solution of a member selected from the group consisting of cyanoethyl and hydroxyethyl amine salts of polyacrylic acid, drying the treated substrate, and then heating the treated substrate at an elevated temperature until the amine salt is substantially all converted to the corresponding amide.

3. The process of claim 2 in which the treated substrate is heated to a temperature in the range of 140° to 190° C. for a period in the range of 1/2 to 8 minutes.

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U.S. Cl. X.R.

117—138.8, 161; 252—8.8