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3,134,686

**DURABLE ANTISTATIC FINISH AND PROCESS
FOR APPLYING SAME**

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This invention relates to a new durable antistatic finish for synthetic hydrophobic textile materials. More particularly, it relates to a new durable antistatic finishing composition for hydrophobic textile materials, a method of applying said composition to such materials and to such materials characterized by the durable antistatic finish.

In general, textile fibers, yarns and fabrics made from synthetic hydrophobic materials, as for example the nylons, the acrylic fibers, the polyester fibers, acetate fibers and the like become electrostatically charged whenever and wherever friction is applied to them. Therefore many disadvantages are encountered during mill processing and fabricating and more so during the end use of the materials manufactured. Aside from the discomfort to the individual wearing a garment which accumulates static electricity, there is also the serious problem of the attraction of dust and dirt particles which results in the garment having a soiled appearance. This usually causes frequent launderings or dry cleanings resulting in poor fabric life due to degradation caused by detergents and bleaches and the normal abrasion resulting from such processing.

The elimination of the static electricity in fabrics would ease the manufacturers' problems, give more comfort to the consumer, and add greater life to the textile materials. It would also reduce hazardous conditions found in such places as operating rooms or in other places where ignition from static electricity could be dangerous.

Antistatic treatments for hydrophobic textile materials subject to the accumulation of static electricity are not new and have been employed by many in the past. However, many of these treatments have marked disadvantages, typical of which are the following: complicated methods of application, inability to be applied from aqueous media, instability with other chemicals, poor durability of the finish applied when subjected to washing or dry cleaning, discoloration of the fabric, and loss of fabric strength or odor problems during pressing.

In the ever increasing field of man-made fibers subject to the accumulation of static electricity, there is a genuine need for a good, durable antistatic treatment which when properly applied will not impart any important deleterious side effects upon the textile material finished therewith or cause discomfort to the consumer.

Accordingly, it is an object of the present invention to provide an antistatic finishing composition which, when applied to synthetic hydrophobic textile materials subject to the accumulation of static electricity, will impart thereto a durable antistatic finish.

A further object of the invention is to provide an antistatic finish capable of application in a conventional straightforward manner from an aqueous medium and which is compatible and stable with other textile agents and auxiliaries.

It is a still further object of the present invention to provide an antistatic finish which does not discolor fabrics finished therewith, does not reduce fabric strength, and does not result in odor problems during pressing or upon completion of finishing.

These and other objects and advantages of the present invention will become more apparent from the detailed description thereof set forth hereinbelow.

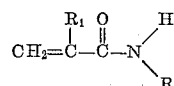
An antistatic agent should be hydrophilic and even hydroscopic in order to attract enough water to the surface of a synthetic fiber to provide a conductive layer so that static electricity can be removed therefrom. In addition, the finish must be water insoluble so that it is not readily removed by laundering or dry cleaning procedures and is therefore durable.

According to the present invention, I have found that a novel combination of a copolymer which is capable of both imparting hydroscopic properties to the surface of synthetic hydrophobic textile materials as well as being capable of cross-linking or reacting with conventional cross-linking agents, when properly applied and cured, results in a durable antistatic finish characterized by most desirable properties and the absence of most of the undesirable properties referred to generally hereinabove.

More particularly, according to the present invention, a process for imparting an antistatic finish to synthetic hydrophobic textile materials is provided which comprises applying (1) a polymer selected from the group consisting essentially of a polymer of an alkali metal ethylenesulfonate and an alkali metal allylsulfonate and mixtures thereof and an acrylamide in which polymer the alkali metal sulfonate and the acrylamide are present in molar ratios of from 3:1 to 1:3, respectively, and (2) a cross-linking agent. The polymer is applied in an amount of from between about 0.25 to about 4% based on the dry weight of the material and the cross-linking agent is applied in an amount of from between about .05 to about 2.0% based on the dry weight of the material. Thereafter, the copolymer and cross-linking agent are cured in intimate association, one with the other, in the presence of a curing accelerator for said cross-linking agent whereby the antistatic finish is durably bound to the hydrophobic textile material substrate.

The term "durable" as employed herein simply relates to the durability of the finish provided by this invention to withstand ordinary washings or household launderings and dry cleaning.

The term "an acrylamide" as employed herein in the instant invention includes compounds of the following general formula:



wherein R_1 is hydrogen, methyl or ethyl and R_2 is hydrogen or lower alkyl containing from 1 to 4 carbon atoms. Preferably the acrylamide employed is acrylamide per se.

The "cross-linking agent" employed in the process of this invention may be any of those cross-linking agents well known to those skilled in the textile finishing art, which are employed to impart crease resistance to cellulosic fabrics. Thus, for example, triazine aldehydes, such as the water-soluble triazine aldehydes described in U.S. Patent No. 2,197,357 and in particular, melamine formaldehyde condensates including those containing from 1 to 6 moles of combined aldehyde and 1 to 6 moles of combined alcohol, preferably methanol. Suitable examples of melamine formaldehyde condensates contemplated for use in the present invention are described in U.S. Patent No. 2,529,856. In addition to the melamine formaldehyde condensates, the guanamine formaldehyde condensates and their alkylated derivatives, as for example, those described in U.S. Patent No. 2,887,409. In addition to these aminoplast materials, such aminoplasts at urea formaldehyde condensates, thiourea formaldehyde condensates, cyclic ureas as, for example, dimethylolethylene urea, 1,2-propylene urea, formaldehyde condensates, 1,3-propylene urea formaldehyde conden-

sates, and their corresponding thiourea condensates may be employed as the cross-linking agent in accordance with this invention. In addition to these, the acetone formaldehyde condensates, polyepoxides, such as diglycidyl ether, the diglycidyl ether of ethylene glycol, and other polyglycidyl ethers of polyhydric alcohols having an epoxy equivalency greater than one, such as are disclosed in U.S. Patents 2,730,427 and 2,752,269, may also be employed. In addition to the above, the urons, as for example those described in U.S. Patent No. 2,373,135, and the triazone formaldehyde condensates, such as are described in U.S. Patent No. 2,304,624, may be employed.

In addition to the above cross-linking agents, such materials as formaldehyde, divinyl sulfone and other cross-linking agents known to those skilled in the textile finishing art may be employed.

The alkali metal sulfonates contemplated for use in forming the polymers employed in the present invention may be the sodium, potassium or lithium salts of ethylene or allylsulfonate, though preferably from the point of view of convenience and economics the sodium salt is employed. In preparing the said polymer, the alkali metal sulfonate and the acrylamide are employed as monomers in such amounts as will produce a polymer in which the components are present in a molar ratio of 3:1 to 1:3, respectively, alkali metal sulfonate to the acrylamide and preferably within a range of 1:1.3 to 1:0.90, respectively.

These polymers may be prepared by reacting suitable amounts of the monomeric materials in either an aqueous or an alcoholic reaction medium employing a suitable polymerization catalyst, as for example a free radical catalyst system at temperatures of from between 30 and 100° C. until a polymer of the desired composition is prepared. Illustratively, polymers contemplated for use in the present invention and their process of preparation will be demonstrated in the examples hereinafter.

In general, the polymers of the instant invention may be described as water soluble materials characterized by molecular weights above 10,000 and preferably above 100,000, or in the range of 10,000 to 500,000 and preferably 100,000 to 500,000.

The alkali metal sulfonate copolymer and the cross-linking agent may be applied to the synthetic hydrophobic textile material by any of the conventional procedures, as for example, immersion, dipping, spraying, padding and the like. After application onto the textile material, it is normally dried, as for example, at temperatures up to 250° F. and then cured at temperatures up to the degradation temperature of the synthetic hydrophobic material. Normally temperatures up to 400° F. depending upon the textile material, may be employed to durably affix the copolymer and cross-linking agent in intimate association upon the textile substrate.

The curing is normally accomplished in the presence of an accelerator or catalyst for the cross-linking agent, which catalyst or accelerator is preferably applied from a treating composition containing the copolymer and the cross-linking agent.

The catalyst utilized may be free acid, acid salt, alkanol amine salts, metal salts, and the like. The concentration of catalysts employed may range from about 0.1 to about 25% or higher based on the weight of solids of the cross-linking agent, depending upon the particular type catalyst employed. Thus, for example, between about 0.1 and about 10% of a free acid, such as phosphoric, tartaric, oxalic, or the like, may be employed, while in the case of ammonium chloride, amounts of from between about 0.5 and about 10% are used. In the case of amine salts including alkanol amine salts such as diethanol amine hydrochloride, from about 1.0 to about 10% are most useful, while with respect to salts such as magnesium chloride, zinc chloride, zinc nitrate and aluminum chloride, amounts of from between 5 and 25% may be em-

ployed. In all instances the concentration of catalyst is based on the weight of the cross-linking agent employed.

The copolymer and the cross-linking agent are applied to the synthetic hydrophobic textile substrate in an amount so as to apply from between .25 and 4% of the polymer and preferably in amounts from between .5 and 2% of the copolymer based on the dry weight of the textile material. The cross-linking agent may be employed in amounts of from between .05 and 2%, though usually in amounts of from between .05 and 1%. Preferably the cross-linking agent is employed in an amount of from between about .10 and .5%, based on the dry weight of the textile material.

In order to illustrate the present invention, the following examples are given primarily by way of illustration. No specific details or enumerations contained therein should be construed as limitations on the present invention except insofar as they appear in the appended claims. All parts and percentages are by weight unless otherwise specifically designated.

EXAMPLE 1

Into a reaction flask equipped with a moderate speed stirrer is entered 60 parts of sodium ethylenesulfonate, 160 parts of ethanol, 0.12 part azo-bis (isobutyronitrile) and 14 parts of acrylamide. The reaction mixture is flushed with CO₂ to remove oxygen and then heated to 56° C. for 25 minutes after which 14 parts of acrylamide and 40 parts of ethanol are then added. The polymerization is run for 18 hours at 55° C. The resulting polymer, being alcohol insoluble, is filtered off. The conversion of monomer to polymer was 80%.

Molar ratio of acrylamide/sodium ethylenesulfonate in the polymer was 0.958/1.0 by analysis.

EXAMPLE 2

From the product of Example 1 a formula consisting of the following was prepared.

Materials used:	Parts by wt.
Product of Example 1 (100%)	8.0
Dimethylolethylene urea (100%)	1.55
AlCl ₃ ·6H ₂ O (100%)	1.2
Non-ionic wetting agent ¹ (100%)	0.8
Water to total of	200.0

¹ Nonylphenol plus 9 mol. ethylene oxide.

Swatches of nylon taffeta were padded through the above solution on a micro-set padder and squeezed to 50% expression, giving 2% solids on the weight of the fabric. The thus treated fabric was dried at 225° F. for 1.5 minutes and then cured for 8 minutes at 300° F. in a circulating hot air oven to obtain a reaction between the acrylamide portion of the copolymer and the cross-linking agent, to give what may be termed hydrophilic, but water-insoluble, finish.

The thus treated swatches were conditioned at 75° F. and 33% relative humidity for four hours after which they were subjected to the antistatic tests (initially and after a series of 18 washings in detergent at 140° F.) described as follows:

- (1) Electrostatic resistivity test—ASTM-76-195
- (2) Cigarette ash test

The cigarette ash test method consists of the following: dry, finely divided cigarette ashes are evenly distributed on a sheet of paper. A folded swatch (2 x 10 inches) of the treated fabric is placed upon several layers of 80 x 80 cotton percale for insulation and then briskly stroked with a glass rod approximately 20 times to induce a static charge into the treated fabric. The stroked-fabric is held horizontally about 2 inches from the ashes and then gradually lowered until the ashes are attracted to the fabric.

Fabric that can be lowered to within 1 to 2 millimeters of the ashes without any attraction is classified as anti-

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static. Any attraction of the ashes by the stroked-fabric is classified as static.

The results of the trials of Example 2 are shown in Table I.

Table I

Treatments	Washes ^a	Ash Test	ASTM-76-1959 Test Log Resistivity ^b
2% solids (OWF)			
Product Ex. 2	none	antistatic	10.9
Do	6	do	10.1-10.2
Do	12	do	10.2
Do	18	do	10.7-10.8
Dimethylol-ethyleneurea+catalyst no copolymer.	none	static	14-15
Untreated nylon	none	do	14-15

^a Agitation type wash 5 minutes at 110° F. in 0.1% detergent. Cotton has a log resistivity of 11.0.

^b Resistivities at 50% RH-25° C. Log resistivity=log of surface resistivity in ohms per square of fabric.

EXAMPLE 3

A mixture containing 10.0 parts (0.007 mole) sodium ethylenesulfonate (A), 2.5 parts (0.035 mole) of acrylamide (B), 40 parts of ethanol and 0.4 part of azobis(isobutyronitrile) was refluxed for 2 hours at 78° C.

Conversion of monomer to polymer=65%.

Molar ratio of monomer in the reaction mixture, A/B=1.23/1.00.

Molar ratio of monomer in polymer, A/B=1.23/1.00.

EXAMPLE 4

From the product of Example 3 a formula consisting of the following was prepared.

Materials:	Parts by weight
Product Example 3	2.0
Dimethylolethylene urea	0.5
AlCl ₃ ·6H ₂ O	0.3
Water to total	100

Swatches of nylon taffeta were padded through the solution to obtain 50% wet pick-up (1% OWF). Drying and curing was carried out in the manner shown in Example 2.

Tests by the cigarette ash method showed this treatment imparted antistatic properties that were durable through >5, but <10, agitation type mild soap washes.

EXAMPLE 5

A mixture of 15.0 parts (0.115 mole) of sodium ethylenesulfonate (A), 7.5 parts (0.106 mole) of acrylamide (B), 20 parts of ethanol and 20 parts of methanol and 0.03 part of azobis(isobutyronitrile) was heated to 50° C. for 5.5 hours.

Conversion of monomer to polymer=66.3%.

Molar ratio of monomers in the reaction mixture A/B=1.08/1.00.

Molar ratio of monomers in polymer A/B=0.54/1.00.

EXAMPLE 6

From the product Example 5 a formula consisting of the following was prepared.

Materials:	Parts by wt.
Product of Example 5	4.0
Dimethylolethylene urea	1.35
AlCl ₃ ·6H ₂ O	0.33
Water to total	100.00

Applications were made on nylon taffeta, then dried, cured and tested in the manner described in Example 2.

Antistatic tests performed by the cigarette ash test method showed antistatic properties which were durable to greater than 10 agitator type, mild detergent washes.

EXAMPLE 7

Into a reaction flask equipped with a mechanical stirrer, a condenser and thermometer is entered 20 parts of sodium

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ethylenesulfonate, 3 parts of acrylamide, 11 parts of water and 3 milliliters of a 10% solution of ammonium persulfate. The flask is flushed with CO₂ to remove the oxygen and 4 milliliters of isopropanol is added. The mixture is then heated to 55-60° C. while moderate stirring is maintained. After stirring one hour at the aforementioned temperature, 2 parts of acrylamide is then added and washed in with 2 parts of water. This addition is again repeated after an additional hour of stirring. One hour after the second addition, 3 parts of acrylamide is then added and washed in with 1 milliliter of water and 1 milliliter of a 10% ammonium persulfate solution.

The polymerization is then maintained at 60-65° C. for an additional three (3) hours, to produce a highly viscous solution. This viscous solution is diluted to 200 milliliters with hot water (temperature 70-75° C.). Then 20 milliliters of the dilute solution is treated with 200 milliliters of methanol. The precipitated polymer, free of monomer, weighed 2.35 grams or a conversion of 78.3%.

Molar ratio of monomers acrylamide/sodium ethylenesulfonate=0.92/1.0.

Molar ratio in polymers (by analysis) acrylamide/sodium ethylenesulfonate=1.4/1.0.

EXAMPLE 8

The copolymer prepared as in Example 7 was applied at 2% solids (on the weight of fabric) to nylon taffeta by the procedure described in Example 2 using the following pad bath formulation and obtaining 50% wet pick-up.

Copolymer solution (23.5%)	65.0 ml. (7.65 parts of polymer).
Dimethylol ethyleneurea	1.55 grams.
AlCl ₃ ·6H ₂ O	1.15 grams.
Wetting agent ^a	0.76 gram.
Water (to total)	191.0 grams.

^a Nonylphenol plus 9 mol. ethylene oxide.

The treated nylon was then dried for 1.5 minutes at 225° F. and cured for 8.0 minutes at 300° F.

Cigarette ash tests were performed initially and after 35 individual detergent washes at 140° F., resulted in good antistatic properties.

Results in Table II show log resistivity as described in Table I.

Table II

No. of washes:	Log resistivity
None	8.9-9.1
5	8.9-9.0
15	8.9-9.1
25	9.4
35	9.7-9.8

EXAMPLE 9

A mixture of 200 parts (1.535 moles) of sodium ethylenesulfonate (A), 100 parts (1.412 moles) acrylamide (B), 665 parts of methanol and 0.4 part of azobis(isobutyronitrile) was heated at 55° C. for 5 hours.

Conversion of monomer to polymer=52.6%.

Molar ratio of monomer in the reaction mixture, A/B=1.09/1.0.

Molar ratio of monomer of polymer, A/B=0.81/1.0.

EXAMPLE 10

The product of Example 9 was applied to nylon taffeta in combination with dimethylol ethyleneurea, formaldehyde, and a commercially available polyepoxide in a series of applications. As accelerators aluminum chloride, magnesium chloride and zinc nitrate were employed with the first two mentioned cross-linking agents and zinc fluoroborate with the latter. The results showed that the resulting finishes were antistatic.

EXAMPLE 11

Into a suitable reaction vessel which has been sparged

with carbon dioxide 4.5 parts of acrylamide dissolved in 21 parts of water is added. When the acrylamide has dissolved, 30 parts of sodium allylsulfonate monomer and 4.5 parts of ammonium persulfate are added.

Thereafter, 6 parts of isopropyl alcohol is added and the reaction mixture heated to 60° C. After a one-hour period, 3 parts of acrylamide in 4 parts of water are added continuously to the reaction container. After the addition of the 3 parts, an additional 3 parts are added in the same incremental manner.

After an additional hour 4.5 additional parts of acrylamide in 4 parts of water are then added to the reaction mixture and .15 part of ammonium persulfate dissolved in water are also added thereto. This reaction is run for approximately 12 hours and the reaction mixture is diluted to 250 parts by volume by the addition of water.

In the above preparation the acrylamide and the sodium allylsulfonate monomers were charged on a 1:1 molar basis. The resulting copolymer contained 2.68:1 acrylamide to sodium allylsulfonate molar ratio.

EXAMPLE 12

A formulation containing 4% solids of the copolymer prepared as in Example 11, .4% of a non-ionic surface active agent, .8% of a water-soluble dimethylolethylene urea and .6% of aluminum chloride as a curing accelerator for the ethylene urea was prepared.

This formulation was applied to nylon taffeta so as to impart 2% solids of the copolymer thereon. The so finished taffeta was dried for 2 minutes at 225° F. and cured for 8 minutes at 300° F.

The finished samples were laundered in an automatic washer employing the delicate cycle, which employs warm water (approximately 120° F.) and a low water level. One gram of an anionic detergent per liter of water is employed during the wash cycle.

The fabrics so finished, after being conditioned for at least 24 hours at 33% relative humidity employing the cigarette ash test, using carbon particles, demonstrated that an antistatic finish durable through more than 30 such washes has been produced.

While the present invention has been described principally with respect to the use of a particular class of copolymer and cross-linking agent to impart a durable antistatic finish, this novel composition may be employed with other textile agents and auxiliaries, as for example lubricant softeners, special finishing agents, as for example bactericidal agents, and the like. In addition, other monomeric materials may be introduced into the polymer, which monomers do not destroy or significantly reduce the desirable qualities of the polymers of this invention or the compositions in which they are employed.

While the present invention has been demonstrated primarily by application to formed fabric, it will be appreciated that the polymer and cross-linking agent may be applied to textile materials subject to the accumulation of static electricity whether the material be a filament, fiber or a fabric and whether the fabric be knitted, woven,

felted or otherwise formed. Obviously blends of synthetic hydrophobic fibers with other fibers such as cotton and the like which are not subject to the accumulation of static electricity are contemplated, since the composition of this invention has application to substrates which as a whole develop static electricity.

This application is a continuation-in-part of my co-pending application, Serial No. 151,454, filed November 10, 1961, and now abandoned.

I claim:

1. A process for imparting a durable anti-static finish to synthetic hydrophobic textile materials subject to the accumulation of static electricity which comprises applying thereto a polymer selected from the group consisting of a polymer formed from an alkali metal ethylenesulfonate and an alkali metal allylsulfonate and mixtures thereof and an acrylamide, in which polymer the sulfonate and acrylamide are present in molar ratio of from .3:1 to 3:1, respectively, and a cross-linking agent, said polymer being applied in an amount of from between about 0.25 to about 4% based on the dry weight of the material and said cross-linking agent being applied in an amount of from about .05 to about 2% based on said weight of said material and thereafter curing said polymer with said cross-linking agents in intimate association in the presence of a curing accelerator for said cross-linking agent.

2. A process according to claim 1 in which polymer, the sulfonate and acrylamide are present in a molar ratio of 1:1.3 to 1:0.9, respectively.

3. A process according to claim 1 in which the polymer is applied from between about 0.5 to about 2% based on the dry weight of the material.

4. A process according to claim 1 in which the cross-linking agent is dimethylol ethyleneurea.

5. A process according to claim 1 in which the hydrophobic textile material is nylon.

6. A process according to claim 1 in which the hydrophobic textile material is an acrylic fiber.

7. A synthetic hydrophobic textile material having a durable antistatic finish thereon comprising an insoluble, heat-cured intimately associated composition of a polymer selected from the group consisting essentially of a polymer of an alkali metal ethylenesulfonate and an alkali metal allylsulfonate and mixtures thereof and acrylamide in which the sulfonate and acrylamide are present in molar ratio of .3:1 to 3:1, respectively, and a cross-linking agent, such finish comprising from between about .25 and about 4% of said copolymer and from between about .05 and 2% of said cross-linking agent.

8. Nylon textile material according to claim 7.

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