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3,090,704

**ANTISTATIC AND ANTISOILING AGENT AND
PROCESS FOR TREATING SYNTHETIC LINEAR
TEXTILE THEREWITH**

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This invention relates to a textile treating composition and textile material processed therewith. More specifically the invention relates to a textile treatment to provide antistatic and and antisoiling properties.

The new synthetic textile fibers, for example those prepared from polyethylene terephthalate, hexamethylene adipamide, and polyacrylonitrile, as well as others of the polyester, polyamide, and polyacrylic types, possess many desirable properties which have made them commercially acceptable for many end uses, both alone and in various combinations within themselves and with the natural fibers. However, the hydrophobic character of these new fibers makes them susceptible to the development and retention of static electrical charges. This characteristic of developing a static charge is so objectionable in some instances that it has completely prevented otherwise acceptable fibers from penetrating some important markets.

In addition to the static problem, the new hydrophobic fibers have been found to pick up oily soil much more readily than the older hydrophilic fibers and also to retain the soil more tenaciously during washing and dry cleaning.

Although many antistatic and antisoiling treating agents have been disclosed in the art, none of these have been satisfactory from the standpoint of both effectiveness and permanence of effect. In particular, no treating agent has been disclosed which may be applied to a hydrophobic fiber or fabric, and which will remain on the fiber through the many fabric processing steps as well as the washing and cleaning treatments which are given to the finished garment by the user. Furthermore, many of the antistatic treating agents are found to adversely affect the handle of the fabric, either imparting objectionable stiffness or disagreeable tactile properties.

It is, therefore, an object of this invention to provide textile fibers and fabrics having permanent antistatic surface characteristics. A further object is the provision of synthetic fibers and fabrics having a surface resistant to the pickup and retention of oily soil. Another object is the provision of a novel antistatic antisoiling coating composition which does not require a heating step for curing the coating onto the fiber.

These objects are obtained by this invention which provides an antistatic, antisoiling coating comprising a new class of vinyl terpolymers containing in the polymer molecule (1) a crosslinkable component, (2) an anionic component, and (3) a component containing a strong nonionizable, non-hydratable permanent or induced dipole. Particularly efficacious results are obtained when the terpolymer is applied to the textile material along with a crosslinking agent.

Surprisingly, when the coating composition of this invention is applied to a textile fiber and allowed to dry thereon, either at room temperature or at an elevated temperature, the fiber not only takes on an antistatic character but also is found to resist pickup and retention of oily soil. Furthermore, these advantages are achieved without the loss of any of the desirable physical properties of the fibers, for example those which affect fabric handle and wash-wear properties.

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The meritorious nature of this invention is emphasized by the fact that it is operable upon fibers of polyethylene terephthalate which have hitherto defied all efforts to impart to them durable antistatic antisoiling coatings without adversely affecting other desirable fiber properties. Effective antistatic and antisoiling properties are also imparted to other polyester fibers as well as to other hydrophobic fibers such as those prepared from the polyamides and polyacrylics.

The terpolymers of this invention may be prepared by polymerizing a mixture of (1) a polymerizable vinyl monomer containing a curable methylol or epoxy group, (2) a polymerizable vinyl monomer containing an anionic group, and (3) a polymerizable vinyl monomer taken from the class consisting of (a) acrylate and methacrylate esters from alcohols containing less than 5 carbon atoms, (b) vinyl esters of aliphatic acids containing 2 to 4 carbon atoms, (c) 4- and 5-carbon aliphatic hydrocarbons containing two conjugated double bonds, (d) and styrene.

As indicated, the terpolymers used in this invention must contain a reactive group which enables the terpolymer to be crosslinked after it is applied to the textile material. Epoxy groups and methylol groups are preferred. Epoxy groups may be introduced into the vinyl terpolymer component of the coating composition of this invention by using, as one monomer during an interpolymerization reaction, compounds containing at least one oxirane or 1,2-epoxy group and at least one polymerizable, ethylenically unsaturated bond. Suitable epoxide-containing monomers are exemplified by glycidyl methacrylate, 4-vinylcyclohexane oxide, allyl glycidyl ether, butadiene monoepoxide, vinyl 2,3-epoxy butyrate, and similar compounds. Alternatively, epoxide groups may be introduced into an existing polymer by standard epoxide-producing reactions carried out at reactive centers on the polymer. Examples of such reactions are oxidations of a double bond with hydrogen peroxide, perbenzoic acid, peracetic acid or ozone and treatment of a halohydrin with strong base. In addition, epoxide groups may be attached to a polymer by coupling reactions involving an epoxide-containing molecule and reactive centers on the polymer. An example of said coupling reaction would be the known interreaction of epichlorohydrin with an hydroxyl group of a polymer, producing a glycidyl group joined to the polymer.

For some purposes, N-methylol acrylamide is an excellent crosslinking component. Alternatively, it may be desirable in certain situations to use acrylamide as the crosslinking component and subsequently convert it to N-methylol acrylamide by treatment with formaldehyde.

The anionic component of the vinyl terpolymer may be provided by employing anionic copolymerizable monomers in the interpolymerization reaction which prepares said terpolymers. The anionic monomers may generally be organic acids or they may be salts of organic acids having a pKa value between 0.4 and 2.5. In a preferred terpolymer, the anionic component is the alkali metal salt of an aromatic sulfonic acid. Alternatively, vinyl sulfonates may be used. Specific examples of preferred anionic component monomers include potassium styrene sulfonate, sodium styrene sulfonate, sodium isopropene sulfonate, sodium ethylene sulfonate, triethanolamine styrene sulfonate, and the like. Both alkali metal and alkaline earth metal salts as well as amine salts may be used. Anionic groups may alternatively be introduced into a terpolymer by chemical treatment of reactive centers in a nonionic polymer.

Although the organic sulfonic acids and sulfonate salts are preferred in preparing the vinyl polymers of this invention, it is to be understood that their phosphoric

acid analogs may be used with equally advantageous results.

Carboxylic acids and their salts are not effective as components of the terpolymers of this invention.

In addition to the anionic component and the cross-linking component, the terpolymer of this invention must contain a third component of the class described in order to obtain adequate durability of the antistatic antisoiling coating. From the class of acrylate and methacrylate esters, only those from alcohols containing less than 5 carbons have been found to be useful. One may use, for example, methyl acrylate, methyl methacrylate, ethyl methacrylate, ethyl acrylate, propyl methacrylate, N-butyl acrylate, tetrafluoropropyl acrylate, and "Cello-solve"¹ acrylate. Vinyl esters having somewhat longer carbon chains may be used. Of the vinyl esters useful as third components in the terpolymer of this invention may be mentioned vinyl acetate and vinyl butyrate. Excellent results are also obtained if the third component of the terpolymer of this invention is chosen from 4- and 5-carbon aliphatic hydrocarbons containing a conjugated double bond system, such as, for example, isoprene and chloroprene. Alternatively, the third component may be chosen from monomers such as styrene and substituted styrenes.

The new vinyl terpolymers are preferably prepared in an aqueous emulsion polymerization system using free radical catalysts. The polymerization process may be carried out batch-wise or in a continuous reactive system whereby steady state concentrations are maintained during polymerization. Emulsifying agents such as those commonly used in vinyl type polymerizations may be present to stabilize the terpolymer emulsion formed. Alternatively, solution polymerization procedures may be used.

The use of a suitable catalyst in the preparation of the terpolymer component is usually desirable in the polymerization step in order to obtain a reaction speed which is commercially feasible. The various water-soluble peroxygen compounds are particularly suitable in the practice of this invention as are water-soluble aliphatic azo compounds. For example the various peroxides, e.g., urea peroxide, hydrogen peroxide, potassium peroxide, sodium peroxide and the like may be used, or azo-bis-isobutyramide hydrochloride. Other suitable catalysts include sodium persulfate, potassium persulfate, sodium perborate, peracetic acid and the like. Still other catalysts such as complex catalysts made from a ferrous or ferric salt and hydrogen peroxide as disclosed in U.S. Patent No. 2,508,341 may be used. It is also possible to employ water-insoluble oxygen-yielding catalysts such as benzoyl peroxide, tertiary butyl hydroperoxide, lauryl peroxide and acryl peroxide, and azo compounds. The concentration of catalysts employed is usually very small, e.g., from about 1 to about 20 parts of catalyst per 1000 parts of the reactive mixture. If an inhibitor be present, up to 5% or even more of the catalyst may be necessary according to the concentration of the inhibitor. It is preferable that a neutral initiator or one operable in the pH range 3 to 9 be used in this type of polymerization in order to prevent the premature opening of the epoxide rings of the epoxy-containing monomer.

In the preparation of the terpolymer component for this invention by means of emulsion polymerization where it is desirable to use an emulsifying agent, it is preferred to employ an emulsifier which is not cationic in order that the emulsifier will not detract from or interfere with the formation of an anionic copolymer. Suitable compatible emulsifiers which may be used may be selected from the following types: diamyl, dihexyl, or dioctyl sulfosuccinic esters and salts thereof, salts of alkylated naphthalene sulfonic acids, sulfonated or sulfated higher alcohols, e.g., lauryl sulfate, the salts of the

sulfonated or sulfated higher alcohols, sulfonated oils, glycol oleates and linoleates, mineral oil sulfonates, aromatic sulfonates, wax acid soaps, triethanolamine soaps such as the oleate, monoglycerol linoleate, amino sulfonates and sulfates, ammoniacal or other alkaline caseins, soaps, lecithin, cholesterol, saponin, emulsifying gums such as gum arabic, gelatin, or one of the nonionic polyethylene oxide types. Obviously, various mixtures of these emulsifiers and wetting agents may be employed in order to obtain suitable stability of the emulsions. The present invention is not limited to the use of any particular proportion of emulsifying agent. In general it is preferred to use from 1 to 5% of the emulsifying agent based on the weight of the monomers to be emulsified, but commercially attractive stable emulsions may be obtained if this figure is varied from 0.1% to 25%. The optimum concentration depends primarily upon the materials to be emulsified although other factors such as agitation have a decided effect.

Although the relative amounts of the three monomers present in the terpolymers of the present invention may vary over wide ranges, it is generally desirable, for adequate resistance of the treated fibers to the buildup of static charges and to soiling, for the proportion of anionic monomer to be between 40 and 80% of the total weight of the terpolymer. Optimum adhesion of the coating to the fiber and optimum durability of the coating to laundering, dry cleaning, and weathering is generally provided by maintaining the proportion of the crosslinking component between 2 and 15% of the total weight of the terpolymer and the proportion of the third component having a nonionizable dipole grouping between 10 and 50% of the total weight of the terpolymer.

Many of the monomers operative in the preparation of satisfactory terpolymers may not possess equally matched reactivities so that the polymer compositions obtained may not always coincide with the weight distribution of the monomer feed. But by suitable polymer analyses and adjustments of the monomer feed stream, satisfactory process corrections can be made. In the preparation of the terpolymers of the present invention, stepwise addition of monomers may be employed to obtain segmented block or graft polymer structures which are also satisfactory in the practice of the present invention.

The terpolymers of this invention may be applied directly to textile materials without further modification and cured by heat alone. Alternatively, a catalyst such as zinc fluoborate may be added in order to cure the terpolymer at a lower temperature. However, superior results are obtained, both from the standpoint of permanency of effect and the elimination of the necessity for curing at a high temperature, if the terpolymer is applied to the textile materials along with a crosslinking agent. Best results are obtained if the crosslinking agent is chosen from the polyamines.

The term "polyamine" is intended to include both polymeric amines and monomeric amines having two or more primary or secondary amine groups. The use of amines as curing agents for epoxy polymers is well known and many examples are known in the art. Best results with the coating composition of this invention are obtained when the amine molecule contains at least three primary or secondary amine groups. Examples of suitable amines are diethylene triamine, "Versamid" 125 (General Mills amine-containing polyamide), triethylene tetramine, tetraethylene pentamine, polyethylene imine, ERL-2793 (Bakelite Co. trademark for aliphatic amine-glycidyl adduct), and ZZL-0814 (Bakelite Co. trademark for aliphatic amine-ethylene oxide adduct).

Suitable amine crosslinking agents are also described in British Patent 809,257.

Alternatively, a polyisocyanate may be used as a crosslinking agent, particularly if a tertiary amine catalyst is added. If the terpolymer contains an epoxide group, it

¹Trademark of Union Carbide Corporation for its 2-ethoxy ethanol.

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is sometimes desirable to first treat with ammonia and then effect crosslinking by means of a polyisocyanate, or by a polyaldehyde as, for example, polyacrolein.

The amount of crosslinking agent (e.g., polyamine) required in the coating composition of this invention will depend somewhat upon the terpolymer composition and the structure of the particular crosslinking agent used. In general, with polyamines, best results will be obtained with a ratio of amine hydrogen to epoxy groups in the range 1:4 to 4:1, with ratios in the range 1:2 to 2:1 being preferred.

The coating composition is generally applied to fibers and fabrics from an aqueous dispersion. The term "aqueous dispersion" is intended to mean that the active ingredients of the coating composition are either dissolved in or suspended in a liquid medium which is at least 75% water. The dispersion may be a true solution, an emulsion, or the like. Other solvents which may be mixed with the water of the dispersing medium in amounts up to 25% include the alcohols, ketones, and water-soluble esters. For example, the dispersing medium may contain up to 25% tertiary butanol, acetone, methanol, or dioxane.

The terpolymer and crosslinking agent may be applied to the textile material from separate dispersions in consecutive steps, in any order, with excellent results. However, in most circumstances, it is preferred to use a single dispersion containing both the terpolymer and the crosslinking agent.

In the application of the treating composition to a textile fiber, filament, fabric, or other form of the textile material to be treated, the composition is applied in amount to give the desired antistatic and antisoiling properties. This amount may be very small, as within the range 0.2 to 5% of the weight in the textile being treated. Larger proportions than 5% are unnecessary and uneconomical. In commercial treatments, ordinarily about 0.5 to 3.0% of the treating composition is used based on the weight of the textile material. The amount required varies with the kind of textiles treated and is less, although within the broad range stated, for materials which are less hydrophobic than polyhexamethylene adipamide and polyethylene terephthalate which are particularly susceptible to receiving a static charge and to picking up oily soil.

The effects of the development and retention of a static charge in a textile fabric are apparent to the wearer of the fabric in the clinging of the garment to the wearer and in the pickup of lint. A laboratory test which correlates well with actual wearing experience consists of measuring the direct current resistance of the fabric at 50% relative humidity. High values expressed as the logarithm (base 10) of the resistance in ohms (termed log R) indicate that the fabric will readily acquire and retain a static charge. Conversely, a low value indicates that the fabric will not readily acquire and retain a static charge.

Static was also measured in some cases by applying a high voltage to sample and measuring the time for half of charge to decay to ground and atmosphere ($t_{(1/2)}$). Control polyethylene terephthalate fabrics give >2400 sec. in this test. Values of 200 sec. or less indicate good static performance as evidenced by freedom from static in subjective tests.

The following examples are cited to illustrate the practice of this invention and are not intended to limit the scope thereof.

EXAMPLE I

Methylmethacrylate (25.8 grams) is mixed with glycidyl methacrylate (8.2 grams) in a beaker. 5.0 grams of Igepal CO-880 and 0.5 gram of glycerol monooleate emulsifiers are added to 566 ml. distilled or deionized water in a Waring Blendor and emulsified for about 10 minutes. While the Waring Blendor turns at a moderate rate of speed, the mixed monomers are added to the

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Blendor, followed by sodium styrene sulfonate (66.2 grams containing 17% water of hydration). After approximately 10 minutes of vigorous stirring, the charge is transferred to a 3-neck 500 ml. round bottom reaction flask equipped with a mechanical stirrer, an inlet for nitrogen, and a reflux condenser. Stirring is started and 0.3 gram of potassium persulfate (0.3% based on monomers) is added. The system is deaerated with nitrogen, and 0.1 gram of sodium bisulfite (0.1% based on monomers) is added. Polymerization is conducted for 4 hours at 45° C. under a blanket of nitrogen and is complete after this time. The emulsion obtained is stable for a period of several months and the polymer is shown to have retained active epoxide groups. A portion of the emulsion is coagulated by evaporation to dryness, and the coagulated polymer is washed and dried. The amount of polymer obtained indicates approximately 100% yield. Since the conversion is almost theoretical, the terpolymer composition corresponds to the monomer feed ratio of 29 parts of methylmethacrylate/62 parts sodium styrene sulfonate/9 parts glycidyl methacrylate, and is confirmed by sulfur analysis which indicated $59 \pm 3\%$ combined sodium styrene sulfonate.

The coating composition is prepared by adding to the terpolymer emulsion 11% of "Versamid" 125 triamine, based on the weight of the terpolymer, and diluting the mixture to the required solids concentration.

EXAMPLE II

150 grams of recrystallized anhydrous sodium styrene sulfonate, 30 grams of methylmethacrylate, and 20 grams of freshly distilled glycidyl methacrylate are dissolved in a buffered (pH 6.5) solution of water/t-butanol, 80/20, to make a 25% solids solution, and 0.3% (based on weight of inhibited monomers) of α, α' -azodiisobutyroamidine hydrochloride initiator is added. The solution is flushed with nitrogen, sealed under nitrogen and heated with agitation at $64 \pm 1^\circ$ C. for 4 hours.

The coating composition is prepared by adding 11% "Versamid" 125 (based on weight of solids) to the terpolymer solution, and diluting to the required solids concentration.

EXAMPLE III

A plain weave taffeta fabric woven from polyethylene terephthalate yarn is immersed in the coating composition of Example I, diluted to a concentration of 2% solids, squeezed to 100% wet pickup, and allowed to dry at room temperature.

The fabric sample is tested for static propensity in the laboratory and is found to have a log R less than 7. The durability of the coating is shown by the fact that after boiling the sample in 1% sodium hydroxide for 1 hour the log R has increased only to 8.9. This is in contrast to values of log R greater than 15 exhibited by untreated samples of the same fabric.

The durability of the coating to repeated commercial launderings is shown as follows: Fabrics were submitted to a commercial laundry for washing by the same procedure used for cotton shirts, including pressing. After 5 wash-press cycles, the sample still had a log R of 12.4 compared to >15 for a similarly treated control.

Comparison of the treated fabric samples with control samples reveals that the antistatic coating has had no adverse effect on fabric drape, handle, wrinkle resistance, or crease recovery properties.

EXAMPLE IV

Fabric samples prepared as in Example III were tested for resistance to soiling in the following manner: The test sample along with untreated control was submitted to a commercial laundry for 10 wash-press cycles in the "family wash" classification. Reflectances of the samples were measured before and after laundering. The untreated control decreased from 86 to 82% reflectance

from redeposition of soil from the laundry liquor while the treated sample only decreased from 86 to 85% R.

EXAMPLE V

Using the procedure of Example I, a series of terpolymers are synthesized and used to prepare antistatic coating compositions. These compositions are evaluated as to utility in imparting antistatic properties to tropical fabrics of the hydrophobic fibers listed in Table I. The antistatic coating compositions are applied by immersing the fabric sample in the liquid dispersion, squeezing to give 100% wet pickup on the fabric, and then drying in air at room temperature for 15 minutes, followed by airing at 140° C. for 5 minutes. Similar results were obtained from fabrics that were simply allowed to dry at room temperature overnight.

The treated samples are subject to the static propensity test, described previously, with the results shown in the table, measured both before and after laundering and dry cleaning. (See Table I.)

EXAMPLE VI

A copolymer is made by the process of Example I except that the anionic monomer is not used. To the emulsion obtained is added 11% of "Versamid" 125 and the mixture is diluted to 2% solids. Fabric samples of polyethylene terephthalate are treated with this mixture as in Example II. The treated samples are found to be lacking in the antistatic and antisoiling properties exhibited by those samples of Example III.

EXAMPLE VII

A copolymer, 80/20, sodium styrene sulfonate/glycidyl methacrylate, is made by the process of Example I except that methyl methacrylate component is omitted. To the emulsion obtained is added 22% of an amine-containing

EXAMPLE VIII

To an aqueous dispersion containing 2% by weight of the vinyl terpolymer sodium styrene sulfonate/methyl methacrylate/glycidyl methacrylate (60/30/10) is added 5% on the weight of the terpolymer of Bakelite Co.'s modified amine crosslinking agent ERL-2793. This mixture is used to coat a polyethylene terephthalate tropical fabric following the general procedure of Example III, allowing the coating to cure at room temperature. The coated fabric is subjected to a series of 10 wash-press cycles, following which the fabric is found to have a charge decay rating $t_{1/2}$ of 125 seconds. The untreated control exhibited a $t_{1/2}$ value of greater than 2400 seconds.

EXAMPLE IX

A sample of polyethylene terephthalate tropical fabric is immersed in a 0.5% aqueous solution of polyethylene imine, squeezed to 100% wet pickup, and heated at 140° C. for 5 minutes. The dry fabric is then treated with a 2% aqueous dispersion of sodium styrene sulfonate/methyl methacrylate/glycidyl methacrylate (75/15/10) and cured at 140° C. for 5 minutes. After a series of 20 standard dry cleanings, the fabric is found to exhibit a log R value of 10.1. After a series of 10 launderings, a similar sample exhibits a log R value of 12.6. These results are in contrast to the log R values greater than 15 for untreated control fabrics of polyethylene terephthalate following similar laundering and dry cleaning treatments.

The above procedure is repeated in reverse order first applying the vinyl terpolymer and then applying the polyethylene imine, with similar results.

EXAMPLE X

120 grams of recrystallized sodium styrene sulfonate, 60 grams of methyl methacrylate, and 20 grams of freshly

Table I
EVALUATION OF VARIATIONS IN COATING COMPOSITION

Experiment No.	Terpolymer Composition (wt. percent)			Polyamine		Molar Ratio	After Scouring		After 20 Dry Cleanings		After 10 Launderings	
	Epoxy Monomer (GMA)	Anionic (SSS)	Alkyl (MMA)	Agent	Wt. percent, OWP		Log R	$t_{1/2}$, sec.	Log R	$t_{1/2}$, sec.	Log R	$t_{1/2}$, sec.
1.....	10	60	30	"Versamid" 125.....	11.0	1/1	10.2	1	11.1	1	11.5	12
2.....	7.5	60	32.5	do.....	8.25	1/1	9.7	1	12.3	2	-----	-----
3.....	5.0	60	35	do.....	5.5	1/1	10.0	1	12.0	1	-----	-----
4.....	2.5	60	37.5	do.....	11.0	1/4	10.4	1	12.9	10	-----	-----
5.....	10	75	15	do.....	11.0	1/1	9.6	1	11.8	1	11.3	1
6.....	10	75	15	Diethylene triamine.....	~1.5	1/1	9.2	1	13.0	1	-----	-----
7.....	10	75	15	Polyethylene imine.....	~2	1/1	9.2	1	12.7	1	-----	-----
8.....	10	30	60	"Versamid" 125.....	11.0	1/1	11.7	~10	-----	-----	-----	-----

Notes:

1. Log R and $t_{1/2}$ measured at 35-38% RH.
 2. Most of coatings were cured 140°/5' although similar results have been obtained from cures ranging from room temperature/24 hours to 160°/15'.
 3. All coatings were applied to tropical fabric.
 4. Polyamine concentrations ranging from 2.75 to 22% OWP have been found to give useful coatings.
- OWP=on weight of terpolymer.
GMA=glycidyl methacrylate.
SSS=sodium styrenesulfonate.
MMA=methyl methacrylate.

polyamide ("Versamid" 125) and the mixture is diluted to 2% solids. Fabric samples of polyethylene terephthalate are treated with this mixture as in Example III. The treated samples are found to exhibit both antistatic and antisoiling properties, but these properties are more rapidly lost upon repeated commercial laundering than for the terpolymer. Log R was 13.2 after 5 wash-press cycles compared to 12.4 for sodium styrene sulfonate/methyl methacrylate/glycidyl methacrylate (60/30/10) "Versamid" 125.

When the process of this example is repeated leaving out the epoxy component, glycidyl methacrylate, instead of the methyl methacrylate, the antistatic-antisoiling properties imparted to the fabric are found to be of extremely poor durability. Static protection is almost completely lost in a single wash cycle.

distilled glycidyl methacrylate are emulsified in 1121 ml. of distilled water buffered at pH 6.5. Emulsification is effected by high speed stirring with 10 grams of Igepal CO-880 emulsifier and 1 gram of glycerol monooleate emulsion stabilizer. After 0.17% (based on monomer weight) of α,α' -azodiisobutyroamidine hydrochloride initiator and 0.10% dodecyl mercaptan chain transfer agent is added, the system is flushed with nitrogen, and heated at 64° C. for 3 hours, after the normal induction period, under nitrogen and with stirring. The resulting dispersion contains 15% solids and has a viscosity of approximately 240-260 centipoises measured at 24° C. A portion of the dispersion is diluted with water to 4% solids and padded onto a polyethylene terephthalate fabric. The fabric is squeezed dry to give 100% wet pickup and is then dried at 150° C. for 15 minutes. The resulting

fabric exhibits excellent resistance to the build-up of static charges.

The above fabric treating procedure is repeated adding to the terpolymer dispersion 1 part by weight of General Mills' amine-containing polyamide "Versamid" 125 for each 8 parts of terpolymer. The resulting coated fabric not only has high initial resistance to the build-up of static charge, but is found to retain this property through at least 10 repeated standard launderings. Static protection is exhibited even at low humidities and after washing in calcium rich (hard) water.

EXAMPLE XI

A series of vinyl terpolymers is prepared following the procedures previously described. Aqueous dispersions of these terpolymers are applied to fabrics prepared from a polyethylene terephthalate copolymer containing 2 mole percent of 5-sodium sulfoisophthalic acid. The terpolymer coatings are cured by heating the fabric to 140° C. for 5 minutes. The treated fabric samples are then tested for antistatic performance after an initial scouring treatment and again after a series of simulated commercial launderings. The results of these tests are summarized in the following table. The abbreviations used in the table are:

SSS—sodium styrene sulfonate;
NBA—normal butyl acrylate;
TFPA—tetrafluoropropyl acrylate;
CA—"Cellosolve" acrylate;
VA—vinyl acetate;
VB—vinyl butyrate;
I—isoprene;
C—chloroprene;
S—styrene;
MMA—methyl methacrylate;
GMA—glycidyl methacrylate.

Table II

Coatings	Scoured		Log R After X Simulated Commercial Launderings			Per- cent Dura- bility to 1st scour
	Per- cent load	Log R	4X	5X	10X	
SSS/NBA/GMA; 75/15/10	1.06	10.0	11.0	-----	12.1	65
SSS/TFPA/GMA; 75/15/10	1.37	9.5	10.2	-----	11.7	61
SSS/CA/GMA; 75/15/10	1.09	9.8	10.7	-----	12.7	69
SSS/VA/GMA; 75/15/10	0.83	<9.0	-----	10.2	12.4	60
SSS/VB/GMA; 75/15/10	0.66	<9.0	-----	10.2	11.7	39
SSS/I/GMA; 75/15/10	1.29	9.1	10.0	-----	11.4	75
SSS/C/GMA; 82/7/11	0.83	9.5	10.8	-----	12.7	52
SSS/S/GMA; 75/15/10	1.16	9.6	10.3	-----	12.0	73
SSS/MMA/GMA; 75/15/10	0.96	9.2	-----	10.0	11.0	63
SSS/MMA/GMA; 60/30/10	1.33	9.3	-----	9.7	10.0	72
SSS/MMA/GMA; 50/40/10	0.65	10.7	-----	11.9	11.8	36
SSS/S/GMA; 50/40/10*	1.11	11.3	-----	11.6	-----	65

*Tested on fabric of polyethylene terephthalate homopolymer.

The above experiments are repeated with the exception that to the dispersion of terpolymer is added 1 part of "Versamid" 125 for each 8 parts of terpolymer, and the coated fabric is allowed to dry at room temperature overnight rather than being heat cured. The results of static propensity tests are summarized in Table III below. It is seen that the presence of the amine crosslinking agent not only eliminates the necessity for heat curing but also increases the durability of the coatings to scouring.

Table III

Coatings	Scoured		Log R After X Simulated Commercial Launderings		Per- cent Dura- bility 1st Scour
	Per- cent Load	Log R	5X	10X	
SSS/NBA/GMA; 75/15/10	3.00	12.1	11.6	11.9	99
SSS/TFPA/GMA; 75/15/10	2.92	12.6	12.1	12.5	100
SSS/CA/GMA; 75/15/10	3.09	12.1	11.6	11.8	100
SSS/I/GMA; 75/15/10	1.88	11.3	11.1	11.5	100
SSS/C/GMA; 82/7/11	3.21	10.7	10.6	11.1	96
SSS/S/GMA; 75/15/10	3.27	11.2	10.8	11.2	99

(See abbreviations for Table II.)

A most important aspect of this invention is the fact that the coating composition containing an amine curing agent may be applied and dried onto a fiber or fabric at room temperature with good results. Alternatively, the coated fiber may be heated to accelerate curing, if desired.

An unexpected advantage of the antistatic coating compositions of this invention is the fact that fabric which have been treated with said coating may be subjected to standard dry cleaning treatments without picking up mahogany oil soaps, widely used by many dry cleaning establishments. Many previously tested antistatic coatings did not offer this advantage and mahogany oil soaps were picked up, causing the fabrics to become yellow and stiff. Notorious examples of such polymeric coatings are those whose antistatic behavior is based primarily upon ether groups such as polyethylene oxide groups and those whose antistatic behavior is based upon cationic groups such as amine and quaternary amine groups. Thus, it is obvious that the coatings of this invention offer a marked improvement over those of the prior art.

Although the coating compositions of this invention have been described in terms of application to filaments, yarns, warps, knitted fabrics, and woven or nonwoven fabrics, they also may be applied to other shaped articles such as films, rods, bristles, and the like. The coating composition may be applied by spraying, roller coating, brushing, dipping, or other suitable means.

As many variations of this invention will be apparent to those skilled in the art without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. As a new article of manufacture a synthetic linear polymer fiber having a superficial coating of a terpolymer prepared by polymerizing a mixture of (1) a vinyl monomer containing a curable group selected from the class consisting of methylol and epoxy groups, (2) a vinyl monomer containing an anionic group, and (3) a vinyl monomer selected from the class consisting of (a) acrylate and methacrylate esters of alcohols containing less than about 5 carbon atoms, (b) vinyl esters of aliphatic acids containing 2 to 4 carbon atoms, (c) 4 and 5 carbon aliphatic hydrocarbons containing two conjugated double bonds and (d) styrene.

2. The article of claim 1 in which a 1,2-epoxy group is present during the polymerization.

3. The article of claim 2 in which the epoxy compound is glycidyl methacrylate.

4. The article of claim 1 in which the vinyl anionic component is a sulfonate.

5. The article of claim 4 in which the sulfonate is a styrene sulfonate.

6. The process which comprises applying to a synthetic linear polymer fiber a terpolymer prepared by polymerizing a mixture of (1) a vinyl monomer containing a curable group selected from the class consisting of methylol and epoxy groups, (2) a vinyl monomer containing an

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anionic group, and (3) a vinyl monomer selected from the class consisting of (a) acrylate and methacrylate esters of alcohols containing less than about 5 carbon atoms, (b) vinyl esters of aliphatic acids containing 2 to 4 carbon atoms, (c) 4 and 5 carbon aliphatic hydrocarbons containing two conjugated double bonds and (d) styrene. 5

7. The process of claim 6 in which a 1,2-epoxy group is present during the polymerization.

8. The process of claim 7 in which the epoxy compound is glycidyl methacrylate. 10

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9. The process of claim 6 in which the vinyl anionic component is a sulfonate.

10. The process of claim 9 in which the sulfonate is a styrene sulfonate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,687,404	Robinson	Aug. 24, 1954
3,000,690	Murdoch	Sept. 19, 1961