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ANTISTATIC TREATMENT OF HYDROPHOBIC TEXTILE MATERIAL

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This invention relates to textile finishing agents. More particularly, it relates to amine-modified polymeric esters capable of being cross-linked on textile fibers to provide durable finishes which enhance the valuable properties thereof, and to a process for applying these finishes to fibers and fabrics.

This invention has for one of its objects the provision of a novel method of imparting durable anti-static properties to hydrophobic fibers and textiles. By the term "durable," is meant that these anti-static properties are not eliminated upon repeated washing of the fibers or fabrics under usual conditions of laundering or dry-cleaning.

Another object of this invention is to provide what is known in the art as a "lofty" hand while, at the same time, circumventing the accumulation of static electricity on textile fibers. Still another object of this invention is to provide a means of dyeing cellulosic fibers such as cotton or rayon, as well a hydrophobic fibers, with acid dyes. Other objects of this invention will become apparent from the following description.

Textile materials prepared from hydrophobic fibers accumulate electrostatic charges by friction or rubbing, e.g. in processing where the filament or fiber and its assemblies are led over guides, or in weaving, or even in use and wear. Synthetic hydrophobic fibers have a comparatively low capacity to retain moisture in comparison with such fibers as cotton, wool, and rayon. Such hydrophobic fibers include nylon, e.g., those made of nylon 66 which are prepared by condensation of 1,6 hexamethylene diamine and adipic acid; those made of nylon 6 which are prepared by polymerization of 6-amino caproic acid; "Orlon" acrylic fibers, "Orlon" being a trademark of the E. I. du Pont de Nemours & Co., prepared by polymerization of acrylonitrile; "Dacron" polyester fibers, "Dacron" being a trademark of the E. I. du Pont de Nemours & Co., prepared by condensation of terephthalic acid and ethylene glycol; cellulose triacetate fibers, marketed under the trademark "Arnel" by the Celanese Corporation of America; "Dynel" fibers, "Dynel" being a trademark of the Union Carbide Chemicals Co., which are copolymers of acrylonitrile and vinyl chloride; "Acrilan" fibers, an acrylic fiber, "Acrilan" being a trademark of the Chemstrand Corp.; and other synthetic fibers such as those of polypropylene and the like.

The accumulation of electric charges is assumed to be due to the inability of textile materials to dissipate the charges as fast as they are generated by friction. In processing, accumulation of electrostatic charges may cause yarn ends to stick or tangle severely on machines. Charged fabrics may attract and hold tenaciously lint and soil, and they are often difficult to cut and sew.

The imperative need for a durable textile finish which will impart the property of dissipating electrostatic charges or of preventing their acquisition by hydrophobic fibers and fabrics and which will withstand repeated launderings and dry-cleanings is well known. Finished garments of electrostatically charged fibers have a tendency to cling to the body rendering them uncomfortable to the wearer. Spark discharges may also occur and constitute a significant hazard in some instances, such as in a surgical operating room, in electronic research laboratories, etc.

It is thus apparent that the durable elimination of the tendency of hydrophobic fibers to acquire a static electric charge is often a matter of serious concern to the comfort and well-being of the wearer and even to the safety of those who, although protected themselves by wearing properly finished clothing, are obliged by virtue of their daily work to encounter static charges built up by friction against untreated hydrophobic fabrics.

It is known that impregnation of hydrophobic textile materials with certain water-soluble hydrophilic compounds reduces the tendency of these textiles to accumulate electrostatic charges. Such compounds are the essential constituents of anti-static agents or finishes. Practically all such finishes known to date, however, are removed by laundering, dry-cleaning, or by simply rinsing with water.

Imparting durable anti-static characteristics to hydrophobic fibers, however, has proven to be a most difficult task. There are, at the present time, no satisfactory durable anti-static textile finishes available except for a very few which are obtained by cross-linking polymeric amines. Such finishes, together with processes for applying them to textiles are covered, for example, in co-pending U.S. patent applications Serial Numbers 561,365 and 666,234, filed January 25, 1956, and June 17, 1957, respectively. The polyamines of these co-pending applications are prepared by reaction of an aliphatic polyamine or a simple alkyl amine, respectively, with a dihalide or with an analogous derivative of a water-soluble polyglycol.

The products used as finishes in the present invention and which are cured upon the fiber or fabric to impart durable anti-static properties thereto are amine-modified polyesters. They comprise polymeric esters of amino acids which are either water-soluble or which may be made water-soluble upon acidification. Although, under certain conditions, it is possible to prepare such amino polyesters by direct esterification of dibasic amino acids such as aspartic acid, glutamic acid, or their N-substituted alkyl homologs with polyhydric alcohols such as glycols or polyglycols, in general these compounds are preferably obtained by indirect means. For example, an alpha unsaturated dicarboxylic acid may be esterified with a glycol or polyglycol and the unsaturated polyester thus formed may then be reacted with ammonia or with a primary or secondary amine. The ammonia or amine adds across the double bond of the unsaturated ester, thus forming an amine-modified polyester. For example β amino esters are formed by amination of unsaturated polyesters.

The reactions involved are represented by the following formulas:

$$HOOC—C_nH_{2n-2}—COOH+HO—R—OH \quad (I)$$

$$—O—R—O—CO—C_nH_{2n-2}—CO— \quad (II)$$

$$+NHR'R'' \quad (III)$$

$$—O—R—O—CO—C_nH_{2n-1}(NR'R'')—CO— \quad (IV)$$

wherein n is at least 2, and preferably between 2 and 8; R is either the radical of a glycol

$$HO—(CH_2)_{n'}—OH \quad (V)$$

or of a polyglycol

$$HO—[(CH_2)_m—O]_{n''}—(CH_2)_{m'}—OH \quad (VI)$$

R' and R'' are each hydrogen, alkyl, or substituted alkyl radicals; n' is an integer between 2 and 10; m and m' are integers between 2 and 10.

Formulas II and IV above respectively represent one ester unit of a polymeric unsaturated ester and of a polymeric amino substituted ester of the invention.

Alpha-unsaturated dibasic acids which may be used in preparing the intermediate unsaturated polyesters include maleic acid or its anhydride, fumaric acid, itaconic acid, mesaconic acid, citraconic acid and glutaconic acid. Any other alpha-unsaturated dicarboxylic acid such as itaconic acid, glutaconic acid, mesaconic acid, citraconic acid and the like may be employed, preferably one containing between four and ten carbon atoms in the molecule. Hexene-2-dicarbonic acid, ethyl maleic acid, α,β dimethyl glutaconic acid, xeronic acid and iso amyl glutaconic acid are examples of organic acids containing between six and ten carbon atoms and used in accordance with our invention. Mixtures of these acids may be employed and mixtures thereof with such saturated dibasic acids as succinic acid, sebacic acid, phthalic acid and the like may also be used.

Glycols which may be used in preparing the intermediate unsaturated polyesters include ethylene glycol, the propylene glycols, the butylene glycols, the pentanediols, diethylene glycol, polyethylene glycols such as polyethylene glycol 200, polyethylene glycol 400, polyethylene glycol 600, polyethylene glycol 1540 known under the trade name of "Carbowax 1540," a trademark of Union Carbide Chemicals Co., neopentyl glycol and mixed polyglycols containing two or more alkylene radicals such as those which can be derived by conjoint polymerization of ethylene oxide and propylene oxide. We may also use substitution products of the aforementioned glycols in which one or more hydrogen atoms attached to carbon are replaced, for example, by alkyl groups which may be substituent radicals of the listed glycols as containing from one to four carbon atoms. Mixtures of these glycols may also be employed.

The chain propagation of polyesters so prepared may be limited, i.e. the further growth of the polymeric group may be interrupted by some chemical which terminates the chain at a reactive site, by any method known to the art, such as by use of a monohydric alcohol, a monobasic acid, or a monoamine in suitable amount during the esterification reaction.

In general, we may use glycols or polyglycols containing from two to ten carbon atoms in the alkylene radical thereof. We may use glycols such as hexylene glycol and decamethylene glycol and, in general, prefer those glycols or polyglycols which will yield water-soluble products rather than water-dispersible ones. Hence, a preferred embodiment of our invention utilizes polyethylene glycols having a molecular weight of from about 200 to about 1540.

If desired, a polyester which is not of unsaturated nature, but which contains reactive hydrogens, may also be employed for introduction of an amine group by means, for example, of the amino methylation reaction known as the Mannich synthesis. Thus, for example, a polyglycol ester of malonic acid may be used and the active hydrogen of the malonic acid radical may be replaced in whole or in part by an alkyl or aralkyl aminomethyl radical or by a corresponding disubstituted amino radical derived from monoamines or polyamines containing either primary or secondary amino groups and formaldehyde as hereinafter shown in Example 20.

Amino compounds which are suitable for introduction into polyesters according to this invention include aliphatic primary amines such as methyl amine, ethyl amine, propyl amine, isopropyl amine, butyl amine, hexyl amine, 2-ethyl hexyl amine, decyl amine, lauryl amine, stearyl amine and others, aliphatic secondary amines such as dimethyl amine, diethyl amine, diisopropyl amine, di-2-ethyl hexyl amine, dilauryl amine, distearyl amine and others, aliphatic alkylene and polyalkylene polyamines such as ethylene diamine, propylene diamine, 1,3-diamino propane, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 3,3'-bis amino propylamine, and condensation products of the above-mentioned alkylene and polyalkylene polyamines with fatty acids such as butyric acid, octoic acid, lauric acid, palmitic acid, stearic acid or oleic acid. These condensation products may be either amino alkylene amides of the fatty acids employed or they may be alkyl imidazolines formed by ring closure of these amides by continued dehydration.

Aliphatic unsaturated amines such as allyl amine and crotyl amine may likewise be employed if desired. Hydroxyl substituted aliphatic amines may also be used such as monoethanolamine, diethanolamine, and aminoethylethanolamine.

Cycloaliphatic amines may also be employed such as cyclohexyl amine and dicyclohexyl amine. It is thus apparent that the amines which may be used in the present invention include a wide diversity of compounds of the aliphatic and cycloaliphatic series. Aralkyl amines may also be employed, such for example as benzyl amine and the like. Mixtures of amines may also be used. Amines suitable for the purpose of this invention are limited only by their ability to yield water-dispersible or water-soluble products. In general, however, they should contain from 1 to 26 carbon atoms. To use amines having a higher carbon content would render the products too difficult to dissolve or disperse in water. Moreover, we prefer to employ those amines possessing from one to four carbon atoms and from one to three amino groups.

Although reference has been made specifically to amino modified polybasic acids as the essential components of the amino polyesters that are employed by the process of this invention, polyesters derived either in whole or in part from saturated dibasic acids which are modified in turn by one or more monobasic aliphatic alpha-unsaturated acids, such for example as acrylic acid, methacrylic acid or crotonic acid may be used. In such cases, the amines heretofore mentioned are added across the double bond of the monobasic acid radical, in the same way as previously described with respect to the unsaturated dibasic acids. In such instances also, the monobasic unsaturated acids may be present as monoesters or diesters or polyesters of polyhydric compounds bearing two residual hydroxyl groups capable of further resinification, such for example as the monoacrylate of glycerine, the monomethacrylate of trimethylol propane, the monoacrylate of trimethylol propane, the dicrotonate of pentaerythritol or the diacrylate of an ethylene oxide adduct of pentaerythritol.

The following examples illustrate the preparation of intermediate polymeric unsaturated esters to which amines may be added for the purposes of this invention:

Example 1

200 parts of polyethylene glycol 200 and 98 parts of maleic anhydride were refluxed at 125°–128° C. for 9 hours using 1.3 parts of methane sulfonic acid as a catalyst and 72 parts of toluene as an azeotroping solvent. 17 parts of water were removed corresponding to 97% esterification. Toluene was subsequently removed in vacuo. The product was a viscous, dark yellow liquid.

Example 2

100 parts of maleic anhydride and 400 parts of polyethylene glycol 400 were reacted during 14 hours at 127°–130° C. using 1.5 parts of methane sulfonic acid and 150 parts of toluene to remove water as an azeotrope. It is to be noted that instead of using 400 parts of polyethylene glycol 400, 1600 parts of Carbowax 1540 may be used.

Example 3

607 parts of polyethylene glycol 600, 98 parts of maleic anhydride and 1.3 parts of methane sulfonic acid were reacted under azeotroping conditions in the pres-

ence of 194 parts of toluene. Reflux was carried out at 128°–130° C. for 11 hours and water and toluene removed as in Example 1.

Example 4

416 grams of ethylene glycol and 792 grams of fumaric acid were heated while sparging with nitrogen until a maximum temperature of 230° C. had been attained. The product was a viscous liquid having a light yellow color.

Example 5

550 grams of diethylene glycol and 675 grams of itaconic acid were reacted with carbon dioxide as a sparging gas to a maximum temperature of 230° C. Upon cooling, the product was a very viscous, light amber liquid.

Instead of the maleic anhydride used in the preceding examples, we may use equimolar amounts of other alpha-unsaturated dicarboxylic acids such as mesaconic, citraconic or glutaconic acid.

Example 6

200 parts of polyethylene glycol 200, 85 parts of succinic anhydride and 26 parts of crotonic acid were reacted as in Example 1, the product being a viscous, dark yellow liquid. Instead of crotonic acid an equal amount of methacrylic acid may be used. If desired, acrylic acid can also be used to replace the crotonic acid of this example in equivalent amount. Instead of succinic anhydride, 126 parts of phthalic anhydride may be employed.

Example 7

490 parts of maleic anhydride were reacted with 520.5 parts of pentanediol 1,5 in the presence of 10.1 parts of methane sulfonic acid under reduced pressure (30–33. mms.) at a temperature ranging from 80° C.–125° C. during 5 hours. Water was removed during the operation and the product was a light colored, viscous liquid, insoluble in water but soluble upon acidification.

Examples 8 through 19 show the preparation of amino-substituted polymeric esters from the unsaturated polyesters of the preceding examples.

Example 8

To the product of Example 1, 37 parts of diethyl amine was added at 70° C. through a separatory funnel in a drop-wise manner. After addition of all of the diethyl amine, the temperature was raised to 110° C. and held for 2 hours. Unreacted diethyl amine was then removed at 10 millimeter vacuum, raising the temperature to 140° C. during one-half hour. 3 parts of unreacted diethyl amine was removed in this manner. The product was a dark brown, very viscous, water-soluble liquid.

Example 9

37 parts of diethyl amine was added as in Example 8 to the product of Example 2, yielding a dark brown, viscous, water-soluble liquid somewhat lighter in color than the product of Example 1.

Example 10

37 parts of diethyl amine was added to the product of Example 3 under the same conditions as given in Example 8. The product was a light brown, very viscous, water-soluble liquid somewhat lighter in color than the product of Example 9.

Example 11

33 parts of methyl amine gas was passed into 200 parts of the product of Example 4 at a temperature of 30° C. The temperature of reaction rose rapidly to about 80° C. The mixture was stirred after completion of addition of monomethyl amine for a period of one and one-half hours. The product had a molasses-like viscosity

and could be dissolved in water by addition of a small amount of acetic acid or hydrochloric acid.

Instead of the methyl amine, 18 parts of anhydrous ammonia may be used to yield a similar product.

Example 12

93 parts of cyclohexyl amine was reacted with 190 parts of the product of Example 4 under the conditions of Example 10, the product being a very viscous, amber colored liquid which could be dissolved in water by acidification.

Example 13

40 parts of an alkyl imidazoline which was prepared by condensing double-pressed stearic acid with diethylene triamine in an equimolar ratio with removal of two mols of water was reacted with 90 parts of the product of Example 3 at a temperature of 75°–100° C. After one hour of reaction, the product was cooled and was of an orange-reddish color, semi-solid in nature, soluble in acidified isopropyl alcohol-water mixture.

Example 14

300 parts of dipropylene glycol, 200 parts of diethylene glycol and 400 parts of maleic anhydride were reacted in a manner similar to that of Example 4 and to 200 parts of the product was added, under the conditions of Example 13, 30 parts of an imidazoline prepared from equimolar amounts of butyric acid and diethylene triamine. The product was a dark brown, viscous, water-soluble fluid.

Example 15

250 parts of the product of Example 5 was reacted with 40 parts of monoethanolamine under the conditions of Example 12. A viscous, orange-brown fluid was obtained.

Example 16

202 parts of the product of Example 7 was reacted with 36.4 parts of diethyl amine added drop-wise during one-half hour at 60° C. Reaction was then continued for one and one-half hours longer at 120° C. A 15 mm. vacuum was then applied at 120° C. during one and one-half hours, thus removing 3.6 parts of unreacted diethyl amine. The product of this reaction was a water-insoluble, light yellow solid which, upon acidification with acetic acid or hydrochloric acid became water-soluble.

Example 17

202 parts of the product of Example 7 was reacted with 14.6 parts of diethyl amine under the same conditions as in Example 16. 1 part of unreacted amine was removed at reduced pressure. The product was a very light colored solid, water-insoluble, but becoming soluble upon the addition of acid.

Example 18

553 parts of the product of Example 2 was reacted with 14.6 parts of diethyl amine as shown in Example 17, with final removal of 1 part of diethyl amine. The product was a dark viscous, water-soluble liquid.

Example 19

To the product of Example 6, was added 13 parts of dimethyl amine, anhydrous, with cooling. After addition of all the amine, the reaction mixture was allowed to come to room temperature and stand for 24 hours. The product was a dark-colored, viscous, water-soluble fluid.

It is to be understood that the preceding examples are illustrative of the wide diversity of types of chemical compounds which may be used in the process of the invention described hereinafter. Any of the acids, glycols and amines previously mentioned may be employed in making finishes suitable for the process of this invention.

In general the esters to which the amine is added should be relatively low in acid number. We prefer to use esters having an acid number of 30 or less. The esters

should be as nearly neutral as possible. If the degree of acidity of the polyester exceeds an acid number of 30, too much amine will be consumed in making an amine salt. The amount of amine added should not exceed the amount of residual acid of the ester plus the unsaturation in the chain. Likewise, the amount of amine added must be in excess of the amount of residual acidity to be neutralized, but should not exceed the molecular equivalents of the unsaturation present in the chain. A portion or all of the unsaturation may be utilized by amine addition; that is to say, in a polyester containing four double bonds, for example, from one to four mols of amine may be added, as desired, to one mol of polyester.

The following example illustrates the preparation of a suitable amino-polyester from malonic acid by the Mannich reaction:

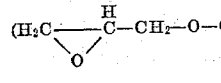
Example 20

104 parts of malonic acid, 400 parts of polyethylene glycol 400 and 2.5 parts of toluene sulfonic acid were added to a three-neck reaction flask fitted with agitator and heated to 140° C. at 20 mm. vacuum. Water vapor removed from the reaction was collected in a condenser cooled with an ice-calcium chloride mixture. After 10 hours, 16 parts of water had been collected, indicating 89% reaction.

To the polymeric ester produced, 15 parts of paraformaldehyde and 10 parts of hydrochloric acid were added at 60° C. 22.5 parts of anhydrous dimethyl amine was then passed under the surface, while stirring, during one and one-half hours at 60° C. At the end of this time, analysis of unreacted formaldehyde showed 90% reaction. The product, a polymeric ester possessing dimethylamino methylene groups replacing hydrogen of the methylene radicals of the malonic acid, was a yellow-colored, viscous, water-soluble paste.

The substantially linear amino polyesters formed according to the preceding description and in accordance with the illustrations of Examples 8 to 20 can be converted into insoluble larger molecular weight compounds by reacting them with bifunctional or polyfunctional cross-linking agents in a ratio of one molecule of amino polyester to at least one cross-linking molecule, thus resulting in a three-dimensional structure. The cross-linking agents capable of forming these three-dimensional insoluble resins from the linear soluble polymeric amino esters described herein include any water-soluble or water-dispersible bifunctional alkylating agent. We prefer to use water-soluble compounds, more specifically, the halides of polyethylene glycols, the halides of water-soluble ethylene oxide-propylene oxide co-condensates, and the di and poly epoxides of polyhydroxy compounds. Less general in their applicability are aqueous dispersions of ethylene dibromide, bischloromethyl naphthalene, and the like.

Among the halides of polyethylene glycols which we prefer to use, may be mentioned the diiodide of polyethylene glycols, having a molecular weight of from 200 to 600, and particularly the diiodide of polyethylene glycol 600. Any other appropriate water-soluble or water-dispersible reactive polymeric glycol dihalide may however be used such, for example, as diethylene glycol diiodide or a mixed polyethylene-propylene glycol diiodide. Reactive dichlorides and dibromides may also be employed. Among the di and poly epoxides which we prefer to use for the purpose of this invention, we may mention specifically the product known in the trade as "Eponite 100" (a trademark of the Shell Chemicals Corp.) which is believed to possess the structure,



and the diglycidyl derivatives of trimethylol propane and trimethylol ethane.

We may also use other diepoxides such as butadiene dioxide, diglycidyl ether, and the diglycidyl ether of p,p' dihydroxy diphenyl methane.

We may also employ compounds containing one or more epoxy groupings and one or more halogens such, for example, as epichlorohydrin.

In carrying out the process of this invention, the polymeric amino-ester heretofore described is dissolved in appropriate amount in an aqueous bath to be used for textile fiber or fabric treatment and a suitable amount of water-soluble cross-linking agent such as polyethylene glycol 600 diiodide or "Eponite 100" is also added to the bath. It will be noted that for the satisfactory performance of the purpose of this invention both polymeric amine and cross-linking agent must be either water-dispersible or water-soluble. We prefer to use water-soluble materials. In some cases, the polymeric amine such as those of Examples 13, 16 and 17 may of themselves not be water-soluble, but water solubility can be induced for the purpose of this invention by addition thereto of a limited amount of either an organic or inorganic acid such, for example, as acetic acid, formic acid, or muriatic acid. The bath thus prepared is then used in the treatment of textile materials.

Depending upon the cross-linking agent employed, we may or may not use various catalysts to facilitate curing. Thus, for example, when diepoxides are employed, we may use catalytic amounts of boron trifluoride or zinc fluoroborate. The selection of appropriate catalysts will be well understood by those skilled in the art.

The goods are impregnated and once treated, are dried and cured at temperatures of approximately 200°–400° F., depending upon time, which may vary from periods of approximately 30 minutes near the lower temperature limit to flash curves of 1 second at the higher temperatures. So-treated hydrophobic fibers such as those previously enumerated may then be after-washed or not, as desired and are found to be incapable of acquiring a static electrical charge even after they have been laundered many times. The number of launderings of which these treated goods are capable without loss of anti-static properties will depend upon the specific nature of the finish and also upon the specific nature of the hydrophobic fiber. Nylon, for example, in general, will retain its anti-static characteristics through 5–10 ordinary commercial launderings at 140° F., whereas Dynel will retain its durable anti-static characteristics when treated with the products of this invention and in accordance with the process thereof through about 25 ordinary commercial 140° F. launderings.

The compounds of this invention when properly applied to hydrophobic textile materials, act as durable anti-static finishes, extremely resistant to washing and dry-cleaning. The appearance and hand of the cloth are not unfavorably affected by the finish. It is, moreover, possible to impart a wide range of properties to the treated cloth (e.g. stiffness, softness, body) by adequately choosing raw materials for the finish applied.

Another extremely useful property of our new finishes is their ability to absorb acid dyes from an aqueous bath and to hold them on the fiber. Use can be made of this property to dye economically textile materials made from hydrophobic or cellulosic fibers which would not normally absorb acid dyes from aqueous solutions. Certain hydrophobic fibers such as polyesters and acrylonitrile polymers can be dyed with known methods only with the aid of high pressure or with the assistance of certain compounds called carriers or with a selected and limited group of dyes. These dyeing methods impose severe limitations on the selection of color and depth of color and they are usually costly.

The new finishes embraced in this invention enable finished fabrics to be dyed by members of the large group of acid or wool dyes at comparatively low cost. Furthermore, the products and process of this invention may also be used in dye and pigment binding with coincident de-

velopment of anti-static properties. This refers to the fixation of water-soluble dyes to prevent bleeding and mechanical binding of water-insoluble pigments.

The outstanding property of these new finishes, however, is to reduce or eliminate the tendency of textile materials comprising hydrophobic fibers and filaments to accumulate electrostatic charges as hereinafter more specifically set forth.

An adequate measure of the ability of the textiles to dissipate charges is their electrical conductivity (or electrical resistivity which is the reciprocal value of conductivity). It is known that a specific area conductance of the textile material higher than 10^{-13} reciprocal ohm (i.e. an area resistivity lower than 10^{13} ohm) is sufficient to consider the textile material as having no objectionable tendency for the accumulation of charges. A higher specific area resistance is usually indicative of the tendency to accumulate charges.

We define the area resistivity of the fabric as its electrical resistance between two parallel metallic electrodes placed at a distance equal to their length. When the distance between electrodes is *n* times their length, the measured resistance must be divided by *n* in order to obtain the specific area resistance. The instruments used to measure electrical resistance are well known, e.g. a Wheatstone bridge may be used, or a strip of fabric is placed between electrodes connected across a device for measuring electric potential (voltage) having a very high leakage resistance and a potential is then applied across the fabric; the source of potential is then disconnected from the electrodes. From the observed rate of discharge of the initial potential and from the capacity of the system the area resistivity can be calculated.

The electric resistance of textile materials depends on their moisture content, which in turn is a function of the relative humidity of the surrounding atmosphere. Therefore, measurement of electrical resistivity of the fabric must be carried out at a known relative humidity level in order to give reproducible results. The measurements indicated in the following examples were carried out at a relative humidity of substantially 30% and at 74° F.

The treatment of textiles by the process of this invention is illustrated by the following Examples 21 and 22. It will be understood that the invention is not limited to the details of these examples, but embraces equivalent processes as described herein, within the limits of processing conditions hereinafter set forth.

Example 21

An undyed, bleached taffeta fabric woven from Dacron polyester yarn was impregnated in a three-roll padder with an aqueous solution containing 100 parts of water and 16 parts of the product of Example 11, acidified with formic acid to a pH of 6.5, and 2.2 parts of "Eponite 100." The cloth was dried for two minutes at 140° F. The dry pick-up or add-on was found to be 2 parts per 100 parts of fabric by weight. Curing was then conducted for a period of five minutes at 320° F. The treated fabric showed a specific area resistance in the order of 10^{10} ohms after 25 launderings in a Westinghouse household washing machine at 140° F. A portion of the same fabric which had not been treated in the manner described showed a specific area resistance greater than 10^{14} ohms. The treated fabric, after many launderings, thus exhibited no objectionable tendency to accumulate electrostatic charge, 10^{13} ohms being a practical dividing line between comfort and discomfort for wearing apparel, with respect to the acquisition of static electricity.

Example 22

A textile treating bath was prepared containing 8 parts of the product of Example 8 and 2 parts of "Eponite 100" dissolved in 90 parts of water and adjusted to a pH of about 6. "Dacron" taffeta was passed through this solution in a padder to a 20% wet pick-up and dried at 200° F. for 5 minutes. The dried fabric contained 2% of added solids on the weight of the goods. It was subsequently cured during 5 minutes at 300° F.

Initial specific area resistance of the treated fabric was 10^{10} ohms. After 10 launderings at 140° F. in a Westinghouse automatic washing machine, using one tablespoon of synthetic detergent ("Tide," a product of the Procter and Gamble Company), the dried fabric showed a specific area resistance of 5×10^{12} ohms. Untreated fabric possessed a specific area resistance between 10^{14} and 10^{15} ohms regardless of the number of launderings.

Instead of an 8:2 ratio of the product of Example 8 and "Eponite 100," we may use ratios varying from 9:1 to 1:1 with substantially similar anti-static performance of the treated goods. In general, we prefer to use a ratio of from 8:2 to 6:4.

The treated fabric of this example possesses an exceptionally pleasing soft and full hand and good retention of initial color. The reflectance of the untreated "Dacron" taffeta as measured by the Photovolt Reflectometer, Model 610, was 101 whereas that of the treated goods prior to laundering was 97.5. Laundering did not materially affect reflectance values.

Example 23

A textile treating bath was prepared in a manner similar to that of Example 22, using a 7:3 ratio of the product of Example 9 and "Eponite 100." "Dacron" taffeta was similarly treated to a dry add-on of 2% by weight of the fabric. Drying and curing conditions were the same as in Example 22. The fabric after curing showed an initial specific area resistance of 10^{10} ohms. After 10 launderings at 140° F. it was 2×10^{12} ohms.

A similar application to a 65:35 Dacron-wool medium weight men's suiting material, applied to a dry add-on of 1% solids, improved initial specific area resistance from 10^{13} for untreated fabric to 1.5×10^{11} for treated material. After 15 dry-cleanings according to the method of Federal specification CCCT 191B, Test Methods 5508, the treated fabric showed a specific area resistance of 3.8×10^{11}. In this instance, the product of Example 9 and "Eponite 100" were used in a 6:4 ratio.

Instead of "Eponite 100" in Examples 22 and 23, a like amount of polyethylene glycol 600 diiodide may be used in a bath adjusted to a pH of 9. Initial results on "Dacron" fabrics so treated showed 10^{9} ohms specific area resistance. In general, fabrics treated with the products of the present invention possess a full and lofty hand.

It will be apparent that any of the products of Examples 8 to 20 may be employed for the treatment of textiles in accordance with the processes of Examples 21 to 23. In general, we may use ratios of from 9 parts of amino polyester to 1 part of cross-linking agent to about 1 part of amino polyester to 1 part of cross-linking agent, regardless of the nautre of the amino polyester or the cross-linking agent. We prefer to employ a ratio from about 4:1 to about 3:2. In general, we may use a textile treating bath containing from about 1% by weight of combined amino polyester and cross-linking agent to about 50% by weight thereof. We prefer to employ from about 5% to about 12%. In general, also, we may use a dry add-on of from about ½% on the weight of the goods to about 8% on the weight of the goods. We prefer to use between from about 1% to about 3%. Depending upon the cross-linking agent used, the pH of the textile treating bath may vary from about 4 to about 11. In general, we prefer to use from about 6 to about 9.

In general, we may use curing times after drying of from about 1 second to about 30 minutes, depending

upon the temperature which will be inversely proportional to the time. We may use temperatures of from about 250° F. to about 400° F. In general, we prefer curing times of from about 1 minute to about 5 minutes with curing temperatures of from about 350° F. to about 250° F.

In general, also, we may use any of the hydrophobic fibers herein above set forth. All hydrophobic fibers behave similarly since the phenomenon is presumably attributable to surface deposition. When the purpose of this invention is to improve dyeing properties of the fabric without regard to anti-static performance, we may also use cotton or rayon. Where it is desired to reduce the anti-static charge which can be acquired by woolen or mixed goods such as in carpeting, we may also use wool fibers.

Blends of any of the preceding fibers may be employed and application may be made to woven or non-woven goods, to tufted and pile fabrics and to knitted goods, felted goods and fibers, both staple and filament.

Application of the anti-static finishes according to the process of this invention may be made from a padder, from a jig, from a dyebox, by spray, or by any other appropriate means.

It will be understood that treatment of textile fibers or fabrics according to the process of this invention may be carried out with addition to the bath of any desired surfactant or textile finish or dye which may be compatible with the anti-static agents of the present invention.

While a preferred method and products are disclosed and exemplified herein, it is understood that various changes as to procedure, arrangement and use of materials may be made without departing from the spirit and scope of the invention as claimed.

We claim:

1. In a process of treating a textile material, the steps of applying to said material an aqueous bath containing a polymeric amino substituted ester essentially consisting of recurring radicals of at least one aliphatic dicarboxylic acid having from 4 to 10 carbon atoms, recurring radicals of an aliphatic compound bearing two hydroxyl radicals and selected from the group consisting of alkylene glycols and polyalkylene glycols, and at least one amino radical selected from the group consisting of primary, secondary, and tertiary amino radicals attached directly to a carbon atom of a radical of an acid selected from the group consisting of aliphatic dibasic acids and aliphatic monobasic acids, said acid being esterified with the aforesaid aliphatic compound bearing two hydroxyl groups; said bath further containing a cross-linking agent selected from the group consisting of dihalides of alkylene and polyalkylene glycols, alkylene dibromide bis chloromethyl naphthalene, and epoxides of dihydroxy and polyhydroxy compounds, said polymeric amino substituted ester and said cross-linking agent being present in the bath in a weight ratio from about 9:1 to about 1:1 and said bath containing, by weight, a total of polymeric amino ester and cross-linking agent of from about 1% to about 50%; and subsequently drying and heating the textile material having said bath applied thereto at an elevated temperature until said polymeric amino substituted ester and said cross-linking agent react to form a compound on said textile material durable to laundering.

2. In a process as set forth in claim 1, said aliphatic dicarboxylic acid being selected from the group consisting of succinic, glutaric, methylsuccinic, and bis(dimethylaminoethyl) succinic acid.

3. In a process as set forth in claim 1, said aliphatic compound being polyethylene glycol having a molecular weight between substantially 200 and approximately 1540.

4. In a process as set forth in claim 1, said aliphatic compound being ethylene glycol.

5. In a process as set forth in claim 1, said aliphatic compound being 1,5 pentanediol.

6. In a process as set forth in claim 1, said aliphatic compound being diethyleneglycol.

7. In a process as set forth in claim 1, said aliphatic compound being dipropylene glycol.

8. In a process as set forth in claim 1, said amino radical being the methylamino radical.

9. In a process as set forth in claim 1, said amino radical being the diethylamino radical.

10. In a process as set forth in claim 1, said amino radical being the propylamino radical.

11. In a process as set forth in claim 1, said amino radical being the unsubstituted amino group.

12. In a process as set forth in claim 1, said amino radical being the cyclohexylamino radical.

13. In a process as set forth in claim 1, said amino radical being an alkyl imidazoline radical.

14. In a process as set forth in claim 1, said amino radical being the ethanolamine radical.

15. In a process as set forth in claim 1, said esterified acid being succinic acid.

16. In a process as set forth in claim 1, said esterified acid being phthalic acid.

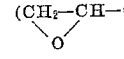
17. In a process as set forth in claim 1, said esterified acid being crotonic acid.

18. In a process as set forth in claim 1, said esterified acid being acrylic acid.

19. In a process as set forth in claim 1, said esterified acid being methacrylic acid.

20. In a process as set forth in claim 1, said cross-linking agent being the diiodide of a polyethylene glycol having a molecular weight of substantially 200 to 600.

21. In a process as set forth in claim 1, said cross-linking agent being an epoxide of the structural formula



22. A textile material coated with the reaction product of the polymeric amino substituted ester with the cross-linking agent of claim 1.

23. In a process of treating a textile material the steps of applying to said material an aqueous bath containing a polymeric amino substituted ester essentially consisting of recurring radicals of at least one aliphatic dicarboxylic acid having from 4 to 10 carbon atoms, recurring radicals of an aliphatic compound bearing two hydroxyl radicals and selected from the group consisting of alkylene glycols and polyalkylene glycols, and at least one amino radical selected from the group of primary, secondary, and tertiary amino radicals said amino radical being attached directly to one of said carbon atoms and said dicarboxylic acid being esterified with said aliphatic compound; said bath further containing a cross-linking agent selected from the group consisting of dihalides of alkylene and polyalkylene glycols, and expoxides of dihydroxy and polyhydroxy compounds, said polymeric amino substituted ester and said cross-linking agent being present in the bath in a weight ratio from about 9:1 to about 1:1 and said bath containing, by weight, a total of polymeric amino ester and cross-linking agent of from about 1% to about 50%; and subsequently drying and heating in textile material having said bath applied thereto at an elevated temperature until said polymeric amino substituted ester and said cross-linking agent react to form a compound on said textile material durable to laundering.

24. In a process of treating a textile material, the steps of applying to said material an aqueous bath containing a polymeric amino substituted ester essentially consisting of recurring radicals of at least one dicarboxylic acid having from 4 to 10 carbon atoms, recurring radicals of a least one monocarboxylic acid having from three to four carbon atoms, recurring radicals of an aliphatic compound bearing two hydroxyl radicals and selected from

the group consisting of alkylene glycols and polyalkylene glycols, and at least one amino radical selected from the group of primary, secondary, and tertary amino radicals, said amino radical being attached directly to one of the carbon atoms of said monocarboxylic acid, said dicarboxylic and said monocarboxylic acids being esterfied with said aliphatic compound; said bath further containing a cross-linking agent consisting of dihalides of alkylene and polyalkylene glycols, and epoxides of dihydroxy and polyhydroxy compounds, said polymeric amino substituted ester and said cross-linking agent being present in the

bath in a weight ratio from about 9:1 to about 1:1 and said bath containing, by weight, a total of polymeric amino ester and cross-linking agent of from about 1% to about 50%; and subsequently drying and heating the textile material having said bath applied thereto at an elevated temperature until said polymeric amino substituted ester and said cross-linking agent react to form a compound on said textile material durable to laundering.

No references cited.