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TEXTILE FINISHING COMPOSITIONS

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U.S. Cl. 260—2 5 Claims

ABSTRACT OF THE DISCLOSURE

A method of imparting durable antistatic finish to hydrophobic materials normally susceptible to accumulating electrostatic charges comprising treating said materials in an acid environment with a hydroxy terminated polyfunctional polyoxyalkylene compound and an acid-catalyzed nitrogen-containing crosslinking agent.

This invention relates to novel compositions used to finish hydrophobic substrates and to substrates produced therein.

More particularly, this invention concerns novel compositions used to impart durable antistatic finishes to hydrophobic textile materials which have a tendency to accumulate static charges.

The expression "hydrophobic textile materials" as used throughout this application refers to synthetic thermoplastics in the form of yarns, slivers, filaments, tows, fibers, articles and garments, and the like produced by drawing, spinning, combing, weaving, knitting or nonwoven procedures. Illustrative hydrophobic textile materials include the preferred polyesters and polyamides, the polyalkylenes such as polyethylene and polypropylene, polyacrylonitrile and the like, as well as the mixtures of one or more of the hydrophobics and/or their blends with natural textiles such as wool and cotton. Rayon for the purposes of this invention is considered to be a natural textile since it is derived from a natural material, cellulose.

Textile materials manufactured from hydrophobic fibers, filaments, yarns, etc., have a relatively low capacity to retain moisture in comparison with their natural counterparts, cotton and wool, and normally tend to accumulate electrostatic charges in their processing during manufacture or during subsequent usage as a textile article or garment. For example, a garment manufactured from untreated hydrophobic materials will cling to the wearer rather than hang smoothly. In order to remove this objectional tendency or reduce it to acceptable levels, a great many antistatic finishes have been developed.

One of the most promising antistatic finishes which has been developed utilizes an alkaline-catalyzed interpolymer of a polyoxyalkylene compound with a polyfunctional amide and a quaternary ammonium salt described in copending Ser. No. 677,090, filed Oct. 23, 1967. This finish provides substantial reduction of the static charge of treated hydrophobic materials as compared to the untreated controls, is compatible with many common textile adjuvants, and is durable to repeated laundering. Unfortunately, the finish causes severe yellowing in white materials and off-shading in colored materials. This yellowing adversely affects the aesthetic appearance of the treated material and can place the finished materials at a competitive disadvantage compared to the same material before treatment. A comparable

finish possessing all of the favorable characteristics of the aforementioned finish which does not cause yellowing would represent a substantial advance in the finishing of hydrophobic materials.

It is therefore an object of this invention among others to provide durable antistatic finishes for hydrophobic materials, particularly polyester and polyamides and their blends with cotton.

Another object is the development of the above antistatic finish which substantially obviates the yellowing and shading problems of previous antistatic finishes.

Yet another object is the production of novel hydrophobic textile materials possessing good hand, durable antistatic properties without comprising the whiteness of undyed materials or the shading of dyed materials.

These objects and many others are attained by treating the hydrophobic substrates with a quantity of a curable antistatic finish, sufficient upon curing to impart an antistatic finish to the treated substrate, when processed according to the procedure described below.

More specifically, a hydrophobic substrate such as polyester, polyamide or the blends with cellulosics, is treated in acidic environment with:

(a) At least one nitrogen-containing polyfunctional polyalkylene,
(b) At least an acid-catalyzed nitrogen-containing crosslinking compound,

then the treated substrate is exposed to elevated temperatures to convert the resultant interpolymer to a water-insoluble film, having a reduced tendency to accumulate electrostatic charges.

In the preferred practice, a hydrophobic fabric or a blend such as polyester-cotton or polyamide-cotton is padded with an acidified aqueous formulation of

(a) A polyhydroxy-polyglycolamine and
(b) At least one acid-catalyzed nitrogen-containing agent,

then dried and cured between about 100 to 200° C. for a sufficient time to form a water-insoluble polymeric film upon the treated substrate and substantially reduce the specific area resistivity of the treated substrate compared to untreated controls.

In order to more easily acquaint the reader with the inventive concept, the following additional description is submitted:

(1) Application conditions

The treating compositions can be in a variety of forms such as solutions, dispersions, emulsions, suspensions and the like. While aqueous formulations are frequently employed, non-aqueous formulations or mixtures of water with various solvents can be used. No particular mode of application is required. Any of the application methods used in the textile industry to treat textile articles are satisfactory. These include padding, dipping, spraying, coating among others. The temperature of application is not critical to success and temperatures ranging from room temperature and below up to the boiling point of the solvent system can be employed if desired. The concentration of reagents in the treating solutions can vary considerably depending upon the wet pickup of the substrate. The critical factor is the "add-on" gain in the dried substrate. Experience has shown that this "add-on" must be at least 1%, and usually 3% or more, based upon the dry weight of the substrate to impart a sub-

stantial reduction in the tendency of the treated, cured substrate to accumulate electrostatic charges. This quantity of "add-on" is referred to as an antistatic imparting amount of finish. Higher quantities of "add-on" while affording satisfactory reduction of electrostatic charges given even greater antistatic durability upon laundering, but tend to adversely affect the hand and add to the cost.

(II) Catalysts

One or more acids or their salts of mixtures of acids and salts serve as satisfactory catalysts for the required catalysis of this invention. Carboxylic acids such as citric acid, and mineral acids such as hydrochloric acid in diluted concentrations can be utilized. Alternatively acidic metallic salts such as zinc nitrate and magnesium chloride can be used by themselves or in conjunction with the acids. No particular quantity of acid need be employed as long as the pH of the system is below 6.0, preferably between about 3.5 and 5.5.

(III) Acid-catalyzed nitrogen-containing crosslinking agents

The acid-catalyzed crosslinking agents employed in this invention are nitrogen-containing resin precursors, particularly those capable of being insolubilized at acid pH values. These resin precursors include those characterized as aminoplast resin precursors, ureaformaldehyde type resins and the substituted cyclic triazines. Suitable groups of resin precursors include dimethylol and polymethylol derivatives of urea, ethylene-urea, propylene-urea, dihydroxyethylene-urea, thiourea, dicyandiamide, guanidine, esters of carbamic acid, the methylolated aminotriazines and methylolated triazines as well as their etherification products. The preferred crosslinking agents are 1,3 - bis(hydroxymethyl) - 2-imidazolidinone, also known as dimethylolethyleneurea, N^2, N^4, N^6 - tris(hydroxymethyl)-melamine, hexahydro-1,3,5 - tris(3 - methoxypropionyl)-s-triazine, and mixtures of these agents.

(IV) Polyfunctional polyoxyalkylene compounds

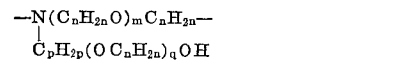
The preparations of these compounds are disclosed in U.S. Pats. 3,351,622 and 3,197,463, and have structures selected from the group consisting of

(1) $(HO\,C_nH_{2n}-)_2N(C_nH_{2n}O)_mC_nH_{2n}N(-C_nH_{2n}OH)_2$

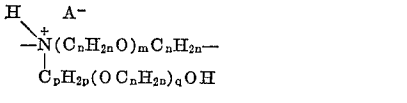
(2) $[(HO\,C_nH_{2n}-)_2\overset{+}{N}H(C_nH_{2n}O)_mC_nH_{2n}\overset{+}{N}H(-C_nH_{2n}OH)_2]\cdot 2A^-$

(3) $[(HO\,C_nH_{2n}-)_3\overset{+}{N}(C_nH_{2n}O)_mC_nH_{2n}\overset{+}{N}(-C_nH_{2n}OH)_3]\cdot 2A^-$

and polymers having recurring units selected from the group consisting of

(4)


and

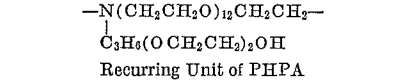
(5)


wherein

A^- is an anion, preferably an anion such as chloride or carboxylate;
m is an integer from 3 to 50, inclusive;
n is an integer from 2 to 4, inclusive;
p is an integer from 2 to 3, inclusive; and
q is an integer from 2 to 20, inclusive.

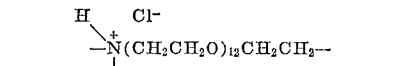
The preferred polyoxyalkylenes are those characterized within Formulas 4 and 5. The following more

specific structures represent the recurring units of polyoxyalkylenes used in this invention:



Recurring Unit of PHPA

and



Recurring Unit of PHPA Hydrochloride

(V) Antistatic interpolymers of this invention

As indicated earlier, the antistatic interpolymers of this invention are prepared by exposing admixtures of polyoxyalkylene reactants such as PHPA, acid-catalyzed crosslinking agents such as hexahydro - 1,3,5 - tris(3-methoxypropionyl)-s-triazine, 1,3 - bis(hydroxymethyl)-2-imidazolidinone, and N^2, N^4, N^6 - tris(hydroxymethyl) melamine, and acidic catalysts to elevated temperatures until insolubilization takes place. The following kinds of reactions are believed to occur during the formation of the insoluble products when PHPA or a suitable salt (as the hydrochloride) is cured with the above crosslinking agents:

(A) A condensation process in which molecules of methanol are eliminated as by-products by reaction between

(1) methoxy groups of hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine, and
(2) active H atoms on hydroxyl groups of molecules of PHPA or PHPA salt.

As a result, PHPA (or PHPA salt) is cosslinked and converted into a so-called 3-dimensional or "ladder" polymer.

(B) A condensation process in which molecules of water are eliminated as by-products by reaction between

(1) hydroxyl groups of 1,3-bis(hydroxymethyl)-2-imidazolidinone, and
(2) active H atoms on hydroxyl groups of molecules of PHPA or PHPA salt.

The net result is an insoluble, infusible, nonlinear polymer.

(C) A condensation process in which molecules of water are eliminated as by-products by reaction between
(1) hydroxyl groups of
N^2,N^4,N^6-tris(hydroxymethyl)melamine and
(2) active H atoms on hydroxyl groups of molecules of PHPA or PHPA salt.
An insoluble complex polymer results.

(D) In addition to the crosslink reaction per se, complex polymers are believed to be formed which contain segments of recurring units resulting from self-condensation of resin precursor. That is, PHPA (which may be in neutralized or partially neutralized form) crosslinked by means of 1,3-bis(hydroxymethyl)-2-imidazolidinone or tris(hydroxymethyl)melamine also may contain blocks or grafted segments of recurring units resulting from condensation polymerization of such reactive resin precursors.

(E) When more than one crosslinking reactant is used in the process, the resulting insolubilized product is believed to have crosslinks stemming from each kind of reactant. Furthermore, the resin precursor may be present in the PHPA-containing product as blocks or grafted segments of polycondensed recurring units.

(VI) Reaction conditions for polymerization and insolubilization of antistatic finish

In order to obtain the desired antistatic finish and to assure its durability to laundering, the finish must be insolubilized by polymerization in an acid environment. Heating is preferred to accelerate the polymerization reaction. The polymerization reaction is usually carried out in the

presence of the hydrophobic substrate by an in situ process. For example, in carrying out the reaction in the presence of a textile substrate, an uncured finish is applied to the substrate to be treated. As indicated earlier, the finish can be in any of several forms. Acidified aqueous solutions are generally preferred for this purpose, although acidification can be done at any time prior to curing. Padding is the preferred form of application. The treated textile substrate is dried preferably between 50 and 105° C. to a moisture content of from about 0.01 to 3.0% by weight moisture, then cured by exposure to elevated temperatures until an insoluble hygroscopic polymer coating is formed.

The temperature at which the polymerization and formation of the insoluble coating takes place can vary considerably according to the reactants, concentrations, pH and catalyst employed. Generally, however, temperatures between about 100–200° C. are preferred.

In order to further described this invention, the following illustrative examples are submitted. Preceding the examples is a description of the test methods employed in evaluating the finish:

(A) Evaluation Test Methods

Laundering: Each laundering was at 60° C. in a household washing machine with a commercial synthetic detergent. The number of laundering-drying cycles (none, 10, 20, etc.) is indicated by No. L, 10L, 20L, respectively, in the tables.

Specific Area Resistivity (SAR): Technical Manual of the American Association of Textile Chemists and Colorists, volume 35, pages 138–139 (1959), Electrical Resistivity of Fabrics, Standard Test Method AATCC 76–1959. The relative humidity was 30% unless otherwise stated. Fabrics having electrical resistivity values greater than 1×10^{13} ohms. are not satisfactorily antistatic, whereas the smaller the value is in comparison with 10^{13} ohms., the more effectively antistatic the fabric is.

Parts and percentages were by weight, unless otherwise noted.

Whiteness (with respect to yellowing), was observed on a subjective comparative basis and rated on a scale of 1 (white) to 25 (severest yellowing, as that resulting from the use of an alkaline catalyst). Whiteness ratings of 1 to 10 were acceptable, with scores of 1 to 5 being best.

(B) ILLUSTRATIVE EXAMPLES

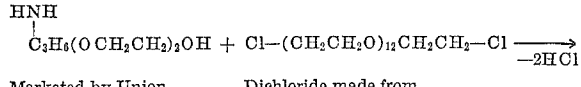
EXAMPLE 1

Acid-catalyzed antistatic finish for white nylon tricot based on polyhydroxy-polyglycolamine (PHPA) with hexahydro - 1,3,5 - tris(3 - methoxypropionyl) - s - triazine (TMPT)

Weighed rectangular portions of white nylon tricot fabric were padded with appropriate aqueous solutions so percentages (on the weight of the fabric) resulted as shown in the following table.

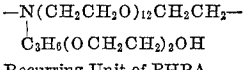
The polyhydroxy-polyglycolamine had been synthesized from

(1) the alkanolamine having the structure shown in the following equation, and
(2) a polyoxyethylene dichloride having the average composition shown:



Marketed by Union Carbide Corp. under the trade name Polyglycolamine H-163

Dichloride made from Polyoxyethylene Glycol 600 (Carbowax 600, Union Carbide Corp.)



Recurring Unit of PHPA, Polyhydroxy-polyglycolamine

Before PHPA was used in the pad bath, enough 5-normal hydrochloric acid was added to the PHPA to lower the pH to 5, in order to insure compatibility.

In the table, TMPT means hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine, and Arquad 12–50 refers to a 50% aqueous solution of dodecyl-trimethyl-ammonium chloride marketed by Armour Industrial Chemical Company.

After the padding step, the treated fabric samples were dried and heated in a forced-draft oven for 3 minutes at approximately 150° C. to bring about formation of an insoluble hygroscopic finish. A whiteness rating was made on each sample prior to washing and also after each sample had been washed in aqueous solution of 0.1% Triton X–100, the trade name of Rohm & Haas Co., for the nonionic wetting agent which is the reaction product of p-(1,1,3,3-tetramethylbutyl)phenol and 9 to 10 mole parts of ethylene oxide, on the average.

The nylon fabric so treated had excellent appearance and durable antistatic properties.

In contrast to the excellent results obtained using an acid-type catalyst (magnesium chloride) with PHPA, TMPT, and Arquad on nylon tricot, results with respect to whiteness were completely unsatisfactory when the acid-type catalyst was replaced by an alkaline one (potassium carbonate). The comparative data are in the accompanying table. (NOTE: Pretreatment of PHPA by HCl was omitted when the alkaline catalyst was used.)

TABLE FOR EXAMPLE 1

White nylon tricot sample No.	Treatment, percent on the weight of the fabric				Evaluation, whiteness rating	
	PHPA	TMPT	Arquad 12-50	Catalyst	Before wash	After wash
2	6.4	0.8	0	0.7 $MgCl_2$	6	1
3	6.4	0.8	1.2	0.7 $MgCl_2$	7	3
4	6.4	0.8	1.2	0.7 K_2CO_3	22	23

EXAMPLE 2

Variation of Example 1 in which A melamine-formaldehyde condensate (Aerotex Resin M–3) was used along with TMPT and PHPA

A weighed rectangular portion of white nylon tricot fabric was padded from an aqueous bath so percentages resulted as follows:

PHPA: 6.4% on the weight of the fabric (OWF)
TMPT: 0.5% OWF (abbreviations as in Example 1)
$MgCl_2$: 0.7% OWF
M–3: 0.5% OWF ("M–3" means Aerotex Resin M–3, a melamine-formaldehyde condensate marketed by American Cyanamid Co.)

As in Example 1, the pH of the PHPA was lowered to 5 before it was added to the pad bath. After padding, heating for 3 minutes at approximately 150° C. was done as in Example 1. The electrical resistivity was good for a durable antistatic finish, greatly reduced the tendency for electrostatic charges to acccumulate on the hydrophobic fabric.

TABLE FOR EXAMPLE 2

Nylon tricot sample	Specific area resistivity, ohms			
	No L	10 L	20 L	30 L
Example 2	2.0×10^{9}	0.9×10^{11}	1.4×10^{11}	1.6×10^{12}
Untreated control	$>10^{13}$	$>10^{13}$		

EXAMPLE 3

Variation of Example 1 in which 1,3-bis(hydroxymethyl)-2-imidazolidinone (DMEU) was used along with TMPT and PHPA

Weighed rectangular portions of white nylon tricot fabric were padded with appropriate aqueous solutions so

percentages resulted as shown in the accompanying table. Before PHPA was used in the pad path, enough 5-normal hydrochloric acid was added to lower the pH of the PHPA to 5. In the table, DMEU means 1,3-bis(hydroxymethyl)-2-imidazolidinone. The padded fabric was heated for 3 minutes at approximately 150° C. Whiteness and antistatic properties were both good.

TABLE FOR EXAMPLE 5

White nylon tricot sample No.	Percent on the weight of the fabric							Evaluation				
	PHPA	TMPT	Aerotex resin M-3	DMEU	HCHO	Arquad 12-50	$MgCl_2$	Whiteness rating	Specific area resistivity, ohms: No L	10 L	20 L	30 L
24	6.4	0.5	0.5	0.5	0	1.2	0.7	2	1.8×10^{9}	0.4×10^{11}	3.5×10^{10}	2.8×10^{11}
25	6.4	0.5	0.5	0.5	0.5	1.2	0.7	4	2.0×10^{9}	0.8×10^{10}	2.5×10^{10}	0.7×10^{11}

EXAMPLE 3

Comparison of various acidic curing catalysts for controlling discoloration on nylon tricot made antistatic by crosslinked PHPA

A procedure similar to that used in Example 1 was followed in padding portions of white nylon tricot fabric. Pad baths were prepared as follows:

Individual 100-gram portions of PHPA were acidified to a pH of 5 by means of the various acids listed in the accompanying table. Each individually acidified portion of PHPA was used to formulate pad baths to which the following ingredients were also added, so the final concentration of each ingredient in grams per liter of aqueous solution was that shown:

Ingredient	Identified in Example—	Grams/liter
Aerotex resin M-3	2	8.0
DMEU	3	12.5
Viva fibreactant [1]	6	40.0
Leucophor WSA [2]	6	8.7

[1] Trade name of Procter & Gamble Co. for a complex reactive long-chain cationic dispersion formulated as a softener for cellulosics and nylon.
[2] Registered trademark of Sandoz, Inc., 61 Van Dam Street, New York, N.Y. 10013, for an optical brightener (a flourescent white dye).

In order to effect drying and curing, each sample was heated at 135° C. for 3 minutes, subjected to high-temperature aging (100° C. for 16 hours) in air. Upon evaluation, all treated fabric samples proved to be durably antistatic. Sample 2, in which phosphoric acid had been used as the acidifying agent, gave the least discoloration and even that very small degree of discoloration was eliminated by washing. Citric acid (Sample 6) resulted in very good whiteness, and hydrochloric acid (Sample 1) resulted in good whiteness. But strong acids exerting a dehydrating or oxidizing action resulted in discoloration to an undesirable degree (sulfuric acid and nitric acid, Samples 3 and 4 respectively). Hence, while various inorganic or organic acids may be used in this invention,

TABLE FOR EXAMPLE 3

White nylon tricot sample No.	Treatment, percent on the weight of the fabric					Evaluation				
	PHPA	TMPT	DMEU	Arquad 12-50	$MgCl_2$	Whiteness rating	Specific area resistivity, ohms: No L	10 L	20 L	30 L
10	6.4	0.5	0.5	1.2	0.7	1	1.3×10^{9}	0.7×10^{11}	1.7×10^{11}	2.0×10^{12}
11	6.4	0.5	0.5	0	0.7	9	1.2×10^{9}	1.0×10^{11}	Not determined	

EXAMPLE 4

Similar to Example 1, but with the melamine-formaldehyde condensate (aerotex resin M-3) and DMEU used in place of TMPT

Weighed rectangular portions of white nylon tricot fabric were padded with appropriate aqueous solutions so percentages resulted as shown in the accompanying table.

Procedural details resembled those of Example 1 (including the comparison test with the alkaline catalyst), except that a combination of melamine-formaldehyde condensate (Aerotex Resin M-3) and 1,3-bis(hydroxymethyl)-2-imidazolidinone (DMEU) replaced TMPA. The padded fabric was heated for 3 minutes at approximately 150° C.

As in Example 1, nylon fabric having the acid-catalyzed finish of PHPA and the combination of reactive products based on amino (or amido) compounds had excellent whiteness and durable antistatic properties, whereas the alkaline-catalyzed finish was unsatisfactory in those respects. Details are in the accompanying table.

TABLE FOR EXAMPLE 4

White nylon tricot sample No.	Percent on the weight of the fabric					Evaluation				
	PHPA	Aerotex resin M-3	DMEU	Arquad 12-50	Catalyst	Whiteness rating	Specific area resistivity, ohms: No L	10 L	20 L	30 L
22	6.4	0.5	0.5	1.2	0.7 $MgCl_2$	3	2.3×10^{9}	2.5×10^{11}	2.8×10^{10}	1.8×10^{11}
23	6.4	0.5	0.5	0	0.7 $MgCl_2$	5	2.6×10^{9}	2.5×10^{10}	2.4×10^{10}	1.1×10^{11}
XX	6.4	0.5	0.5	1.2	0.7 K_2CO_3	23	$>10^{13}$	$>10^{13}$		

EXAMPLE 5

Similar to Example 1, with melamine-formaldehyde condensate (aerotex resin M-3 and DMEU used in combination with TMPT (along with PHPA, as usual)

Weighed rectangular portions of white nylon tricot fabric were padded with appropriate aqueous solutions to yield the "add-on" percentages shown in the accompanying table. Procedural details resembled those of Example 1, except that a combination of three reactive products based on amino (or amido) compounds had been used instead of just TMPA.

Before PHPA was used in the pad bath, enough 5-normal hydrochloric acid was used to lower the pH of the PHPA to 5. In addition to PHPA and the three amino resin precursors in the pad bath, 0.5% of formaldehyde was present also. The padded fabric was heated for 3 minutes at approximately 150° C. Upon evaluation, whiteness and antistatic properties were both good.

strong dehydrating or oxidizing acids are to be avoided. Among organic acids, those of low volatility are preferred

TABLE FOR EXAMPLE 6

White nylon tricot sample	Acid for acidifying the PHPA	Evaluation after curing (135° C. for 3 minutes) and aging (100° C. for 16 hours)				
		Whiteness	Specific area resistivity, ohms			
			No L	10 L	20 L	30 L
1	Hydrochloric	Good	0.5×10^{9}	2.5×10^{10}	3.5×10^{10}	1.4×10^{11}
2	Sulfuric	Poor	0.4×10^{9}	1.4×10^{10}	0.9×10^{11}	0.4×10^{12}
3	Nitric	Poor	1.3×10^{9}	1.4×10^{11}	1.4×10^{11}	1.0×10^{12}
4	Oxalic	Fair	0.7×10^{9}	1.3×10^{11}	2.5×10^{11}	1.6×10^{12}
5	Citric	Very good	1.9×10^{9}	1.1×10^{12}	1.4×10^{12}	1.9×10^{12}

EXAMPLE 7

Comparison of acid-type and base-type catalysts as to durability of antistatic finishes for nylon based on crosslinked PHPA

A procedure similar to that used in Example 1 was followed in padding two kinds of tricot fabric knitted from Nylon 6. Samples of one series (designated by T appended to the sample number) used a texturized fabric made of pre-crimped fibers, whereas the other series of samples (identified with the suffix U for untexturized) were made from fibers which had not been precrimped. Weighed rectangular portions of each kind of nylon fabric were padded with the appropriate aqueous solutions so as to effect the "add-on" percentages (based on the weight of the fabric) shown in the following table.

TABLE FOR EXAMPLE 7

Add-on formula No.	Add-on (in percent) based on the weight of the fabric							Nylon tricot sample No.	Specific area resistivity, ohms	
	PHPA	TMPT	K_2CO_3	Arquad 12-50	Aerotex resin M-3	DMEU	$MgCl_2$		5 L	15 L
71	6.4	0.8	0.7	1.2	0	0	0	71-T	3.4×10^{10}	$>10^{13}$
								71-U	3.0×10^{11}	$>10^{13}$
72	6.4	0	0	1.2	0.5	0.5	0.2	72-T	1.0×10^{11}	1.0×10^{11}
								72-U	1.2×10^{10}	1.7×10^{10}
73	6.4	0.8	0.7	0	0	0	0	73-T	$>10^{13}$	
								73-U	$>10^{13}$	
74	6.4	0	0	0	0.5	0.5	0.2	74-T	6.6×10^{10}	8.0×10^{12}
								74-U	8.4×10^{9}	4.0×10^{10}
Control: Unpadded nylon tricot.								T	$>10^{13}$	
								U	$>10^{13}$	

NOTE.—T=Texturized; U=Untexturized.

In order to effect drying and curing, each padded sample was heated at 135° C. for 3 minutes. The treated samples and controls were evaluated for antistatic activity after 5 and 15 launderings, respectively, as measured by specific area resistivity.

Whenever potassium carbonate (a base-type catalyst) had been used in the formula added to the nylon, the resulting finish was not nearly so durably antistatic as when magnesium chloride (an acid-type catalyst) was used. This can be seen by the data above in the accompanying table.

EXAMPLE 8

Similar to Example 7, but on 100% polyester taffeta

The comparison between acid-type and base-type catalysts demonstrated by Example 7 was carried out on a 100% polyester taffeta, a textile based on another chemical class of man-made fiber. Add-on formulas were those tabulated in Example 7. The suffix V identifies the polyester taffeta samples. Drying-curing was effected by heating each padded sample at 135° C. for 3 minutes. As in Example 7, much more durable antistatic activity resulted from the use of acid-catalyzed finishes as compared to base-catalyzed finishes.

TABLE FOR EXAMPLE 8

Add on Formula No. from Example 7	Polyester taffeta sample No.	Specific area resistivity, ohms		
		5 L	15 L	20 L
71	71-V	3.2×10^{10}	4.0×10^{12}	$>10^{13}$
72	72-V	1.3×10^{10}	7.5×10^{10}	1.7×10^{11}
73	73-V	$>10^{13}$		
74	74-V	1.0×10^{10}	4.5×10^{10}	7.2×10^{10}
Control: Unpadded		$>10^{13}$		

EXAMPLE 9

Similar to Example 7, but on wool fabric

The kind of comparison between acid-type and base-type catalysts demonstrated by Example 9, was carried out on 100% wool fabric which had been dimensionally stabilized through chemical modification by a reactive polymer having terminal aziridine rings. "Add-on" was as tabulated in Example 7. The suffix W identifies the wool fabric samples. Drying-curing was effected by heating each padded sample at 135° C. for 3 minutes. Again, as the data in the table indicate, much more durable antistatic activity resulted from acid-catalyzed finishes than from base-catalyzed finishes.

TABLE FOR EXAMPLE 9

Add-on Formula No. from Example 7	Wool fabric sample No.	Specific area resistivity, ohms	
		5 L	15 L
71	71-W	2.8×10^{11}	$>10^{13}$
72	72-W	8.9×10^{10}	2.8×10^{12}
73	72-W	5.7×10^{11}	$>10^{13}$
74	74-W	6.4×10^{10}	1.0×10^{12}
Control: Unpadded		2.3×10^{11}	$>10^{13}$

EXAMPLE 10

Similar to Example 9, but on worsted fabric

The same kind of durability comparison between acid-type and base-type catalysts demonstrated in Example 9 was carried out on 100% worsted fabric which had been dimensionally stabilized through chemical modification by a reactive polymer having terminal aziridine rings. "Add-on" was as those tabulated in Example 9. The suffix X identifies the worsted fabric samples. Drying-curing was effected by heating each padded sample at 135° C. for 3 minutes. Again the acid-catalyzed finish was shown to be more durable than the base-catalyzed finishes.

TABLE FOR EXAMPLE 10

Add-on Formula No. from Example 7	Worsted fabric sample No.	Specific area resistivity, ohms		
		10 L	20 L	25 L
71	71-X	4.5×10^{11}	1.0×10^{13}	$>10^{13}$
72	72-X	3.1×10^{10}	$13.\times10^{10}$	2×10^{10}
73	73-X	3.3×10^{12}	$>10^{13}$	
74	74-X	2.7×10^{10}	1.5×10^{10}	2×10^{10}
Control: Unpadded		$>10^{13}$		

EXAMPLE 11

Similar to Example G, but on a blend of polyester (55%) and wool (45% by weight)

The comparison between acid-type and base-type catalysts illustrated by Example 7 was carried out on a fabric made from a blend of polyester (55%) and wool (45% by weight). Add-on was as tabulated in Example 7. The suffix Y identifies the polyester-wool fabric samples. Drying-curing was effected by heating each padded sample at 135° C. for 3 minutes. Data again indicated that more durable antistatic activity resulted from acid-catalyzed finishes than from base-catalyzed finishes.

TABLE FOR EXAMPLE 11

Add-on Formula No. from Example 7	Polyester-wool fabric sample No.	Specific area resistivity, ohms		
		No. L	5 L	30 L
71	71-X	2.8×10^{8}	1.1×10^{11}	$>10^{13}$
72	72-Y	8.0×10^{7}	6.8×10^{9}	3.2×10^{9}
73	73-Y	8.0×10^{8}	1.4×10^{11}	$>10^{13}$
74	74-Y	7.5×10^{8}	6.3×10^{9}	4.8×10^{9}
Control: Unpadded		4.1×10^{11}	2.4×10^{11}	$>10^{13}$

EXAMPLE 12

Similar to Example 7, but on a blend of orlon (70%) and wool (30% by weight)

Durability comparisons between acid-type and base-type catalysts were carried out on a fabric made from a blend of Orlon acrylic fiber (70%) and wool (30% by weight) as described in Example 7. [Orlon is a registered trademark of E. I. du Pont de Nemours and Co. (Inc.)]. Add-on was as tabulated in Example 7. The suffix Z identifies the acrylic-wool fabric samples. Drying-curing was effected by heating each padded sample at 135° C. for 3 minutes. Once more the durability of the acid-catalyzed systems were superior to those of the base-catalyzed systems.

TABLE FOR EXAMPLE 12

Add-on formula No. from Example 7	Acrylic-wool fabric sample No.	Specific area resistivity, ohms		
		No L	5 L	15 L
71	71-Z	3.0×10^{7}	2.9×10^{11}	$>10^{13}$
72	72-Z	3.5×10^{7}	5.3×10^{9}	2.7×10^{9}
73	73-Z	4.0×10^{8}	1.4×10^{11}	$>10^{13}$
74	74-Z	3.1×10^{8}	5.7×10^{9}	4.9×10^{9}
Control: Unpadded.		1.5×10^{12}	1.7×10^{12}	$>10^{13}$

As the above examples and discussion indicate, numerous advantages accrue from the practice of this invention. For example, a more durable antistatic finish is provided which does not yellow or adversely affect shading as does the base-catalyzed systems of the prior art. In addition, unlike the antistatic finishes which utilize the insoluble epoxide crosslinking agents, the systems of this invention employ water-soluble nitrogen-containing crosslinking agents. As a result of this there is no need to prepare emulsions or suspensions of variable stability in order to apply the antistatic systems. As a consequence of employing nitrogen-containing crosslinking agents, shelf stability of the formulations is improved, variations in durability are minimized and simpler application and formulation techniques can be used.

Numerous changes and modifications can be made in this invention without departing from the inventive concept. For example, reactants, reaction conditions and substrates can be varied without substantially affecting the desired result. The metes and bounds of this invention are best determined from the claims which follow.

What is claimed is:

1. An insoluble antistatic acid catalyzed interpolymer of a polyhydroxy-polyglycolamine compound selected from the group of compounds represented by the structural formulas:

(1) $(HO\,C_nH_{2n}-)_2N(C_nH_{2n}O)_mC_nH_{2n}N(-C_nH_{2n}OH)_2$

(2) $[(HO\,C_nH_{2n}-)_2\overset{+}{N}H(C_nH_{2n}O)_mC_nH_{2n}\overset{+}{N}H(-C_nH_{2n}OH)_2]\cdot 2A^-$

(3) $[(HO\,C_nH_{2n}-)_3\overset{+}{N}(C_nH_{2n}O)_mC_nH_{2n}\overset{+}{N}(-C_nH_{2n}OH)_3]\cdot 2A^-$

and polymers having recurring units selected from the group consisting of:

(4) $-N(C_nH_{2n}O)_mC_nH_{2n}-$ with $C_pH_{2p}(O\,C_nH_{2n})_qOH$

and

(5) $-\overset{+}{N}(C_nH_{2n}O)_mC_nH_{2n}-$ (H, A^-; with $C_pH_{2p}(OC_nH_{2n})_qOH$)

wherein A^- is an anion, m is an integer from 3 to 50, inclusive, n is 2, 3, or 4, p is 2 or 3, and q is an integer from 2 to 20, inclusive; and acid catalyzed nitrogen containing crosslinking agents selected from the group consisting of hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine, mixtures of hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine with 1,3-bis(hydroxymethyl)-2-imidazolidinone, and mixtures of hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine with melamine-formaldehyde condensates.

2. The insoluble antistatic acid catalyzed interpolymers of claim 1 wherein the crosslinking agent is hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine.

3. The insoluble antistatic acid catalyzed interpolymers of claim 1 wherein the crosslinking agent is a mixture of a melamine-formaldehyde condensate and hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine.

4. The insoluble antistatic acid catalyzed interpolymers of claim 1 wherein the crosslinking agent is a mixture of 1,3-bis(hydroxymethyl)-2-imidazolidinone and hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine.

5. An insoluble acid catalyzed condensation polymer of a polyhydroxy-polyglycolamine compound selected from the group of compounds represented by the formulas:

(1) $(HO\,C_nH_{2n}-)_2N(C_nH_{2n}O)_mC_nH_{2n}N(-C_nH_{2n}OH)_2$

(2) $[(HO\,C_nH_{2n}-)_2\overset{+}{N}H(C_nH_{2n}O)_mC_nH_{2n}\overset{+}{N}H(-C_nH_{2n}OH)_2]\cdot 2A^-$

(3) $[(HO\,C_nH_{2n}-)_3\overset{+}{N}(C_nH_{2n}O)_mC_nH_{2n}\overset{+}{N}(-C_nH_{2n}OH)_3]\cdot 2A^-$

and polymers having recurring units selected from the group consisting of:

(4) $-N(C_nH_{2n}O)_mC_nH_{2n}-$ with $C_pH_{2p}(O\,C_nH_{2n})_qOH$

and

(5) $-\overset{+}{N}(C_nH_{2n}O)_mC_nH_{2n}-$ (H, A; with $C_pH_{2p}(O\,C_nH_{2n})_qOH$)

wherein A^- is an anion, m is an integer from 3 to 50, inclusive, n is 2, 3, or 4, p is 2 or 3, and q is an integer from 2 to 20, inclusive; and hexahydro-1,3,5-tris(3-methoxypropionyl)-s-triazine.

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