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2,820,724

TEXTILE TREATMENT

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No Drawing. Application December 23, 1953
Serial No. 400,095

4 Claims. (Cl. 117—139.5)

This invention relates to the treating of textile materials, particularly so as to render them antistatic without deleteriously affecting their handle.

Many non-cellulosic polymeric substances used in the manufacture of synthetic fibers, such as polyacrylic, polyamide, and polyester compositions, are notably hydrophobic; electrical charges produced on them are slow to flow off or dissipate, especially in atmosphere of low humidity. The presence of electrostatic charges (and resulting forces) along a textile material or between it and its surroundings is unpleasant for both processor and consumer, leading as it does to poor yarn control and enrollment, difficulty in maintaining fabric in register during layout and pattern cutting, and clinging of garments to the person when worn, as well as accumulation of dust by the material at any stage and uncomfortable electrical discharge effects for persons coming into contact with the material.

The literature shows that considerable effort has been expended in an attempt to render the newer textile materials antistatic; however, nearly all the treatments so far devised are non-permanent. Antistatic compositions that are soluble or easily dispersible in water or in the fluids used in dry-cleaning provide some relief for the processor and retailer, but they are relatively useless to the consumer because of their removal from the textile material by washing or dry-cleaning.

Treatment with resins not susceptible to the action of substances used in conventional cleaning procedures (and accordingly herein termed "insolubilizable") has not proved satisfactory heretofore. Most of such resins used for textile treatment do not prevent or reduce the accumulation of electrical charge on the treated material; the few that manage to render the material more or less antistatic when applied in sufficient concentrations impart a harsh boardiness to the material thus treated. Such an unpleasant handle greatly limits the usefulness of textile materials.

A primary object of this invention is treatment of textile materials to render them permanently antistatic. Another object is improvement in resin treatments for textiles so as not to impair the handle of the treated material. Further objects will be apparent from the following discussion.

Attainment of the objects of the present invention is exemplified by use of a composition comprising an aqueous dispersion of a cross-linkable oxygen-containing polyamide, a cross-linking catalyst, and a water-dispersible non-cross-linking polyether. (As used here, "dispersion,"

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"dispersible," and related terms apply to true molecular distribution, i. e., solution, as well as colloidal, or near-colloidal distribution.) When such a composition is applied to a textile material that then is dried, cured, and washed, the textile carries a cross-linked derivative of an oxygen-containing polyamide resistant to washing and dry-cleaning and endowed with antistatic properties, the handle of the textile being substantially unchanged.

To endow a textile material with antistatic properties in the practice of this invention an oxygen-containing polyamide should comprise at least four percent oxygen (by weight), other than that contained in the carbonamide groups, located either intralinearly on the hydrocarbon chain (as in Patents 2,158,064 and 2,191,556) or extralinearly (as in Patent 2,176,074). Usually this oxygen content will be distributed throughout each repeating unit of the polymer structure, although copolyamides in which a minority of the repeating units are free of this oxygen will prove satisfactory if their total content of such oxygen is at least four percent. One-fifth or more of the hydrogen-bearing nitrogen atoms should carry cross-linkable substituent groups. These polyamides need not be sufficiently high in molecular weight to be fiber-forming, though preferably having an intrinsic viscosity of at least 0.3. They should be dispersible in alcohols, in aqueous alcohols, and in water (to an extent depending in part upon the degree of substitution and the oxygen content) so as to be applicable conveniently to textiles from such media.

A conventional cross-linking substituent is an alkoxy-methyl group, which reacts with amide hydrogen to split out the corresponding alkyl alcohol; methoxymethyl is perhaps most readily available, although ethoxymethyl and higher analogues may be used as well. Among suitable cross-linking catalysts for such a substituent are acids of intermediate strength, being as strong as trimethyl acetic acid but not stronger than p-toluene sulfonic acid. Criteria of acidity for this kind of catalyst, along with other examples of suitable catalytic acids, are set forth in Patent 2,430,860.

To be thoroughly satisfactory, the polyether should be water-dispersible, despite heating or other usual circumstances, so as to be removable from the treated material by a conventional scouring operation. For best results, the polyether should have a molecular weight of about 1000 or more. Water-dispersible polyether derivatives, such as a condensation product of ethylene oxide and an alkylated phenol or a polyoxyalkylene derivative of a hydroxyester, wherein the polyether part of the molecule accounts for about 80% or more of the total weight, should prove generally acceptable.

The oxygen-containing polyamide and the polyether may be present in a treating composition of this invention in a weight ratio of from about 10:1 to about 1:10; a range from about 10:1 to about 2:1 appears to give best results. The catalyst is present in comparatively small amount, usually a few percent based upon the combined weights of these two ingredients, or only a few tenths of one percent based upon the weight of the treating composition (including aqueous or alcoholic dispersant), as the composition is usually between about 5% and 15% total solids content. The amount of catalysts depends in part upon the curing temperature and time. The treat-

ment usually should place several percent total solids on the textile material, say a pickup of the bath composition to an extent of from 20% to 200% of the dry weight of the textile material. Specific examples appear below, but many other suitable combinations of ingredients and other conditions in conformity with this invention will be apparent to one skilled in the art.

EXAMPLE I

A. Preparation of oxygen-containing polyamide

Amounts of 73.3 grams purified adipic acid and 67.3 grams purified 4-oxaheptamethylenediamine are dissolved in 140 ml. water. The pH of this solution is adjusted to 7.48 by the addition of adipic acid. A 20 ml. portion then is placed in the glass liner of a pipe autoclave and polymerized according to the following cycle:

- (1) Charge and purged
- (2) Held at 200–210° C. and 250 p. s. i. maximum, 45 minutes
- (3) Raised to 210–250° C., 250 p. s. i. maximum, 30 minutes
- (4) Held at 250° C., 250 p. s. i. maximum, 30 minutes
- (5) Reduced to atmospheric pressure at 250° C., 30 minutes
- (6) Held at 250° C., atmospheric pressure, 30 minutes
- (7) Reduced to pressure equivalent to 2 mm. Hg (or less), 250° C., 30 minutes
- (8) Held as in (7) for 2 hours

The resulting poly-4-oxaheptamethylene adipate exhibits an inherent viscosity of 0.98 in m-cresol solution.

B. Preparation of N-methoxymethyl derivative of polyamide

A three-neck round-bottom flask fitted with reflux condenser, addition funnel, and stirrer is set up in a bath maintained at 60° C. One part poly-4-oxaheptamethylene adipamide from Example I-A is dissolved in two parts formic acid (90% aqueous solution), and 0.3 part methyl formate is added. To this is added a solution consisting of one part formaldehyde (paraformaldehyde and water equivalent to 80% aqueous formaldehyde by weight) and one part methanol, with sufficient sodium hydroxide to effect solution at the boil. Addition is slow for the first minute, then more rapid so that all the solution is added in 3–5 minutes. The reaction mixture is stirred for 19 minutes longer, and one additional part of methanol is added rapidly. After 11 more minutes the reaction mixture is poured into 25 parts of water. The resulting solution is filtered to remove insolubles and is made slightly alkaline with concentrated ammonium hydroxide. A portion of the product precipitates at this point as a viscous paste; precipitation is completed by the addition of salt. The product is separated from the aqueous phase and dried in a vacuum oven over phosphorous pentoxide. The yield is 22.4 grams of N-methoxymethyl poly-4-oxaheptamethylene adipamide from 20 grams of the original polyamide. In the product an average of about one out of every two of the active hydrogen-bearing amide groups is substituted with an N-methoxymethyl group.

C. Preparation of polyether

A particularly useful polyether is prepared by polymerizing 1,2-propylene oxide to molecular weight of 1700 followed by graft polymerization of the product with ethylene oxide to molecular weight of 2200 to give a final product in which about 20% of the ether units are derived from the ethylene oxide. Suitable equipment and procedures for such preparation are known to those skilled in the art; written descriptions may be found in British Patent 610,505 and in Natural and Synthetic Polymers (p. 245) by K. H. Meyer, published in 1950.

D. Formulation of treating composition

An amount of 2800 grams of the N-methoxymethyl-polyamide prepared in Example I-B is dissolved in 10% n-propanol solution composed of 5320 grams n-propanol and 47,880 grams water. To this solution are added 168 grams crystalline citric acid and 2800 grams of the polyether prepared in Example I-C, both of which also go into solution.

E. Treatment of textile material with the composition

Twenty yards each of a plain weave fabric woven from staple yarns spun from polyethylene terephthalate, a 2 x 2 twill fabric woven from staple yarns spun from polyacrylonitrile, and a plain weave fabric woven from continuous filaments of nylon (polyhexamethylene adipamide) are sewn as a strip with suitable leaders at each end to permit processing on conventional textile equipment. The treating composition of Example I-D is placed in the solution tank of a Butterworth paddler and the goods run through at 10 tons pressure on the squeeze rolls. The goods are run through a second time to insure levelness, resulting in a 40–50% wet pickup or approximately 5% solids based on the weight of the fabric (i. e., about 2½% being polyether and 2½% being N-methoxymethyl polyamide). The goods are tented once at 300° F. and 3 Y. P. M. to get a dry fabric, and again at 350° F. and 2 Y. P. M. to cure and insolubilize the N-methoxymethyl polyamide on the goods; these rates correspond to heating time of approximately 1 and 1½ minutes respectively. These high temperatures cause some yellowing of the fabric but the color bleaches out in subsequent washing. The fabrics as removed from the tenter have an unacceptably boardy hand. However, after scouring on a beck at 160° F. in an aqueous bath containing "Duponol" ME (a commercial grade of sodium lauryl sulfate furnished by E. I. du Pont de Nemours and Company, Inc.) for 30 minutes and drying on a tenter, the fabrics have a softened hand nearly equivalent to that of the original untreated fabric. In the washing step the polyether is essentially completely removed from the fabric. (Subsequent experimentation reveals that optimum curing with citric acid requires 2–5% of this catalyst while heating the fabric for 5–7 minutes at 266° F. or equivalent heating for 10–14 minutes at 248° F.) Results of this treatment on the electrostatic charge characteristics of the treated textile fabric appear in Table II below, along with data for the following control treatment and the treatments of additional examples.

F. Control treatment with composition lacking polyether

A treating composition similar to that prepared in Example I-D except for omission of the polyether is used with a run of fabric similar to that described in Example I-E. Given the same treatment, the fabric as it comes from the curing step on the tenter again possesses an unacceptably boardy hand. However, in this instance scouring treatment on the beck does not soften the fabric. A further attempt to soften the fabric by running the goods through a button breaker is unsuccessful, even after ten successive passes.

EXAMPLE II

Amounts of 39.5 grams 3,6-dioxaoctamethylene diamine and 36.7 grams adipic acid are dissolved in 76 ml. water. A 20 ml. portion of this solution, with pH adjusted to 7.5, is polymerized by the cycle described in Example I-A. The product is poly-3,6-dioxaoctamethylene adipamide, which has an inherent viscosity (in m-cresol) of 0.78. Following a procedure like that given in Example I-B, this polyamide is converted to an N-methoxymethyl derivative such that slightly more than 60% of the active hydrogen-bearing nitrogen atoms are substituted with methoxymethyl groups. Continuing simi-

larly to Example I-C, a treating composition is prepared containing 5% N-methoxymethyl poly-3,6-dioxaoctamethylene adipamide, 0.3% crystalline citric acid, and 5% of a polyether prepared as follows: by polymerizing 1,2-propylene oxide to obtain a polyether having a molecular weight of 1700 and, in turn, copolymerizing this product with ethylene oxide to obtain a final polyether having a molecular weight of 8000 wherein 80% of the polyether units are derived from ethylene oxide. This treating composition is applied to fabric according to the procedure described in Example I-E.

EXAMPLE III

Amounts of 55 grams 1,2-bis-(3-amino propoxy)ethane and 45 grams adipic acid are dissolved in 100 ml. water with the pH then adjusted to 7.52. A 20 ml. portion of this solution is polymerized as described in Example I-A. The product is poly-4,7-dioxadecamethylene adipamide with an inherent viscosity (in m-cresol) of 0.39. Twenty grams of this product are treated as described in Example I-B to produce N-methoxymethyl poly-4,7-dioxadecamethylene adipamide in which 65% of the active hydrogen-bearing nitrogen atoms are substituted with methoxymethyl groups; a treating composition is prepared by dissolving this adipamide in water to give a

and Dyeing, Silver Spring, Md. The index of fabric hand (or handle) is a measurement of the bending length according to the hanging-heart procedure described by Pierce in Journal of the Textile Institute 21 T377 (1930).

TABLE I

Example	Polyamide	Percent amide hydrogens replaced with $-\text{CH}_2\text{OCH}_3$	Inherent viscosity in m-cresol
V.....	N-methoxymethyl poly-3-methoxyhexamethylene adipamide.	43	1.05
VI.....	N-methoxymethyl poly-4,7-dioxadecamethylene - 2,5-dioxahexamethylene - 1,6-dicarboxamide.	93	0.95
VII.....	N-methoxymethyl poly-4,7-dioxadecamethylene adipamide/polyhexamethylene - 2,5-dioxahexamethylene - 1,6-dicarboxamide (50/50 mol ratio).	49	0.71
VIII.....	N-methoxymethyl poly-4,7-dioxadecamethylene adipamide.	57	0.92
IX.....	do.....	73	0.92

NOTE.—Based upon 100 parts of solvent (by weight), the treating compositions of these examples contain 5 parts polyamide, 1.25 parts of the same polyether as Example I-C, and 0.3 part citric acid. Water is used as the solvent in Examples VI, VIII, and IX, 15% aqueous n-propanol in Example V, and 10% aqueous n-propanol in Example VII.

TABLE II

Example	Nylon ¹ (Untreated: hand=1.33, ESP=1,700)			Dacron ¹ (Untreated: hand=1.67, ESP=2,000)			Orlon ¹ (Untreated: hand=1.79, ESP=2,000)		
	Hand		ESP	Hand		ESP	Hand		ESP
	Treated	Treated and washed	Treated and 5 washings	Treated	Treated and washed	Treated and 5 washings	Treated	Treated and washed	Treated and 5 washings
I.....	2.03	1.53	400	2.74	1.86	350	2.96	1.91	300
I—Control.....	2.16	2.08	400	2.78	2.43	350	3.01	2.63	350
II.....	1.97	1.48	250	2.66	1.85	250	2.84	1.83	250
III.....	1.85	1.43	300	2.61	1.77	200	2.79	1.97	200
IV.....	1.92	1.51	350	2.73	1.91	300	2.92	2.01	350
V.....	1.81	1.49	400	2.54	1.88	350	2.65	1.86	300
VI.....	1.71	1.38	600	2.06	1.69	800	2.92	1.78	650
VII.....	1.90	1.45	300	2.28	1.87	250	2.53	1.91	200
VIII.....	2.07	1.57	250	2.73	1.82	200	2.95	1.93	250
IX.....	1.76	1.40	250	2.54	1.74	200	2.71	1.84	200

NOTE.—Electrostatic potential (ESP) of all examples after treatment and before washing was 50 volts, except 100 volts for I—Control.

¹ Trademark of E. I. du Pont de Nemours and Company, Inc.

5% solution. Crystalline citric acid is added to give a 0.3% solution, and a polyether prepared by polymerizing ethylene glycol to obtain a molecular weight of 4000 is added to the extent of five percent. Fabric is treated with this composition as described in Example I-E.

EXAMPLE IV

N-methoxymethyl poly-4,7-dioxadecamethylene sebacamide is prepared similarly to the procedure described in Examples I-A and I-B and made into a textile treating composition by dissolving in 10% propanol, adding citric acid, and the same polyether as described (with the same proportions) in Example I-C. This composition then is applied to fabric as described in Example I-E.

Following the procedures previously described, the N-methoxymethyl polyamides and copolyamides listed in Table I below are prepared and made up into the respective treating compositions. These are applied to fabrics made from hydrophobic fibers, such as those described in Example I-E. Properties of fabrics treated with the treating compositions of Examples I, II, III, IV, and the treating compositions of the examples on Table I are summarized in Table II. Textile World 101, No. 1 (January, 1951), pp. 116-7, describes the washing procedures used and the measurement of an electrostatic potential. The dry-cleaning was carried out in standard commercial systems as described in Applied Science for Dry Cleaners published in 1951 by the National Institute of Cleaning

Table II shows the desirable antistatic and handle benefits conferred according to this invention upon three fabrics woven from yarns made (as in E) of representative hydrophobic polymeric materials: Nylon (polyhexamethylene adipamide), "Dacron" polyester fiber (polyethylene terephthalate), and "Orlon" acrylic fiber (polyacrylonitrile). In most instances the compositions exemplified in the table maintained the ESP of the treated fabrics at less than one-fourth of the corresponding untreated values, often one-tenth or less, which suggests the relative improvement from rather high susceptibility to accumulation and retention of electrostatic charges to a comparatively static-free condition, even after five cleanings. Initially unfavorable hand determinations (in the vicinity of 2.0 or higher) produced by application and curing of the respective compositions invariably drop to acceptable readings (near or below 1.8) upon one cleaning. Although the mechanism of the hand restoration is not thoroughly understood, removal of the polyether at the first post-treatment washing apparently breaks up the resinous coating produced on the textile to an extent sufficient to eliminate boardiness but not to such an extent as to preclude the desirable antistatic effect of the remaining resin; of course, no polyether was used in Example I—Control, which accounts for the continued excessive value there in the "hand" column.

The degree of permanence of the antistatic effect of treatment according to this invention depends largely upon

the extent of cross-linking of the oxygen-containing polyamide on the textile treated, while the extent to which the treated material is rendered antistatic depends in large part upon the noncarbonamide oxygen content of the polyamide, as defined previously. Various textile materials require treatments of varying severity. A polyamide containing about five percent non-amide oxygen and having a methoxymethyl substituent on from one-half to three-quarters of its amide groups usually proves satisfactory in a residual amount of a few percent based upon the weight of the textile material. Materials made up of staple yarns generally require less intensive treatment than similar materials comprised of continuous filaments. Polyamide textiles may be protectable at a lower treating level than is appropriate for some of the other hydrophobic materials.

Textile materials of all kinds may be treated successfully according to this invention, whether made of staple fiber or continuous monofilament or multifilaments or any combination of these, and whether in the form of silver, tow, top, individual yarns, yarn sheets, or any kind of fabric, whether woven, knitted, felted, or otherwise formed. The treating composition may be applied by dipping, padding, spraying, or other conventional method, followed by the requisite curing. The textile may be immersed in the treating composition at room temperature with subsequent heating continued throughout removal of the textile from the composition to insolubilize the oxygen-containing polyamide on the textile. Scouring of the treated material removes the polyether or derivative thereof and restores a desirably soft handle to the textile, which will usually have become relatively harsh during the curing step.

Although the usefulness of this invention in providing desired antistatic properties has been emphasized, it is apparent from the description as a whole that the presence of polyether compounds during other resin treatments may be expected to benefit the handle of the treated textile in a similar manner. Not only is this feature of the invention applicable to the treatment of textiles with alkoxymethyl polyamides, regardless of their antistatic properties, but it may be extended also to treatments with

other cross-linkable polymers and with urea-formaldehyde, melamine-formaldehyde, and other resins.

What is claimed:

1. A process for rendering a textile material less retentive to electrostatic charges without adversely affecting its handle comprising treating the textile material with a composition containing an insolubilizable oxygen-containing polyamide, containing at least 4% oxygen by weight exclusive of carbonyl content, and a water dispersible polyether and an insolubilizing agent, insolubilizing the polyamide on the textile material and removing the polyether from the treated textile material.
2. The process of claim 1 in which the polyamide is insolubilized by heating in the presence of a cross-linking catalyst and the polyether is removed by washing with water.
3. The process of claim 1 in which the polyamide is an N-alkoxymethyl polyamide.
4. The process of claim 3 in which the polyether has a molecular weight of at least 1000.

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