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3,123,587

POLYESTER WASH-WEAR FABRIC

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This invention relates to novel fabrics and to the filaments from which they may be prepared. More particularly, it relates to novel polyester fabrics which exhibit dyeability with a variety of dyes as well as excellent "wash-wear" performance, and to the filaments from which the fabrics are prepared.

An objective of the textile industry in recent years has been to provide garments made of fabrics which require minimum care. Desirably, such fabrics are relatively free from wrinkles subsequent to laundering, so that little or no ironing of the fabrics is required. Fabrics which are superior in this regard are frequently described as having good "wash-wear" performance. It has also been desired, of course, that the fabrics be readily dyeable with a variety of commercially available dyestuffs.

In general, the most satisfactory "wash-wear" fabrics have been those made of polyester fibers, such as polyethylene terephthalate fibers. It has also been found that, although the unmodified polyester fibers are not especially versatile with respect to the range of suitable dyestuffs and the depth to which the fibers may be dyed, modifications of the polymer by incorporating copolymeric radicals containing sulfonate salt groups results in fibers which are readily dyeable with basic dyes. Modification of the polyester fiber in this way is more fully described in British Patent 826,248. Unfortunately, however, it has been observed that fabrics made of polyester fibers modified in this way generally exhibit relatively poor wash-wear behavior. The hydrolytic stability of the fibers is also considerably reduced by incorporating the sulfonate salt modifier units in the polymer. Accordingly, there has been a continued search for a new fiber having the properties required for the production of superior wash-wear fabrics.

It is an object of this invention to provide a readily dyeable fabric having good wash-wear properties. Another object is to provide such a fabric which exhibits good hydrolytic stability. A further object is to provide fibers from which such fabrics may be prepared. Other objects will become apparent from the following description and claims.

I have found that these objects are accomplished by a fabric comprised of oriented fibers of a synthetic linear condensation polyester derived from a naphthalenedicarboxylic acid, a glycol from the group consisting of ethylene glycol and p-hexahydroxylylene glycol, and from about 1% to about 5% of a copolymeric ester-forming compound containing a sulfonate salt group. Very good wash-wear performance is exhibited by the fabric of the invention. Surprisingly, the fabric is not only dyeable with basic dyes, but its relative dye uptake with disperse dyes is strikingly higher than that obtained with fabrics derived from the corresponding polyester containing no sulfonate salt group copolymeric units. The hydrolytic stability of the fabrics of the invention is quite good.

The term "synthetic linear condensation polyester" as used herein comprehends a substantially linear polymer of fiber-forming molecular weight comprising a series of predominantly carbon atom chains joined by recurring carbonyloxy radicals,

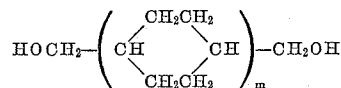


As used herein, the term "polyester" is intended to include

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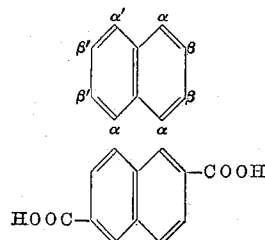
copolyesters, terpolyesters, and the like. Polyesters having a relative viscosity of at least about 8 are considered to be of fiber-forming molecular weight.

The glycols from which the polyesters are predominantly derived are ethylene glycol, p-hexahydroxylylene glycol, or ester-forming derivatives thereof. The p-hexahydroxylylene glycol may be either the cis-isomer, the trans-isomer, or mixtures thereof. These glycols may be represented by the formula

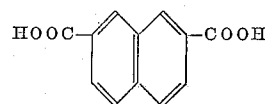


where m is 0 or 1. Preferably, at least 75% of the hydroxyl radicals in the polyester are derived from ethylene glycol or p-hexahydroxylylene glycol.

In accordance with the invention, the acid component from which the polyester is derived is predominantly a naphthalenedicarboxylic acid; preferably, at least 75% is a naphthalenedicarboxylic acid. In a preferred embodiment of the invention, at least 75% of the acid component of the polyester is a β,β' -naphthalenedicarboxylic acid. These acids are characterized by the attachment of one hydroxycarbonyl group to a β -position (2- or 3-position) of one ring in the naphthalene nucleus and the attachment of the other hydroxycarbonyl group to a β' -position (6- or 7-position) in the other ring of the naphthalene nucleus. This positioning of the hydroxycarbonyl groups appears to confer excellent properties on polyesters derived from 2,6- or 2,7-naphthalenedicarboxylic acid or ester-forming derivatives thereof.

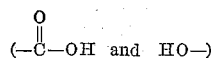


2,6-naphthalenedicarboxylic acid



2,7-naphthalenedicarboxylic acid

The term "ester-forming group," as used herein, refers to either of the complementary radicals, hydroxycarbonyl and hydroxyl



which react with the elimination of water to form a carbonyloxy ester radical



The term also includes functional groups equivalent to the hydroxyl group, such as epoxides or esters, particularly the acetate ester or esters of other aliphatic acids having relatively few carbon atoms, as well as functional groups equivalent to the hydroxycarbonyl group, such as carbonyl halides, anhydrides, salts, and esters with the lower alcohols. Similarly, compounds containing ester-forming groups are designated as "ester-forming compounds." Of course, each of the complementary hydroxycarbonyl and hydroxyl radicals, or functional groups derived from them, must be present in the reaction mixture for polycondensation to proceed; and any excess of one

of the complementary groups with respect to the other is removed during the reaction, usually by volatilization of compounds containing such groups. Glycol esters (hydroxyalkyl esters) of dicarboxylic acids may function in either capacity as ester-forming compounds and thereby function as intermediates from which polycondensation can be initiated directly.

In accordance with the invention, from about 1 to about 5% of a copolymeric ester-forming compound containing a sulfonate salt group is employed in producing the polyester. Such a compound may be represented by the formula



where X is an ester-forming group as defined above, n is 1 or , R is an organic radical, and M is a metal. Potassium 3,5-dicarbomethoxybenzenesulfonate is an example of the compound of the formula, in which X is a carbomethoxy group, n is 2, R is the 1,3,5-trivalent benzene radical, and M is potassium. In general, any metallic element may be employed, examples of specific compounds being the sodium, lithium, calcium, lanthanum, and lead salts of 3,5-dicarbomethoxybenzenesulfonic acid. R is a divalent or trivalent organic radical, depending upon the value of n , and is usually hydrocarbon. However, R may contain substituents which are inert in the polyester reaction mixture. Thus, R may be a halogen-substituted hydrocarbon radical or a chalcogen-containing hydrocarbon radical wherein each chalcogen atom is bonded to carbon or a different chalcogen atom, and no carbon is bonded to more than one chalcogen atom. Examples of suitable compounds include

sodium 1,8-dicarbomethoxynaphthalene-3-sulfonate, potassium 2,5-dicarbomethoxybenzenesulfonate, sodium p-carbomethoxybenzenesulfonate, sodium m-carbomethoxybenzenesulfonate, potassium 4,4'-dicarbomethoxybiphenyl-2-sulfonate, sodium 3-hydroxypropane-1-sulfonate, sodium 4,4-dicarbomethoxy-1-butanedisulfonate, potassium p-hydroxyethoxybenzenesulfonate, potassium 2,5-bis(hydroxyethoxy)benzenedisulfonate, dithium 2-carbo-beta-hydroxyethoxy-5-hydroxyethoxybenzenedisulfonate, sodium 2-chloro-3,5-dicarbomethoxybenzenedisulfonate, and sodium 2-bromo-3,5-dicarbomethoxybenzenedisulfonate.

hydrolysis of the carbonyloxy linkages in the polyester chain. A portion of acid component of the polyester may be comprised by the copolymeric ester-forming component containing the sulfonate salt group, if this component is derived from a carboxylic acid. The remainder of the acid component of the polyester, up to about mol 25%, may be any suitable dicarboxylic acid or hydroxycarboxylic acid. Examples of such compounds include terephthalic acid, isophthalic acid, 4,4'-sulfonyldibenzoic acid, 4,4'-bibenzoic acid, 4,4'-benzophenonedicarboxylic acid, 1,2-bis(4-carboxyphenyl)ethane, bis-4-carboxyphenyl ether, 4-(2-hydroxyethyl)benzoic acid, and 4-(2-hydroxyethoxy)benzoic acid.

The following examples are cited to illustrate the invention, although they are not intended to be limitative.

EXAMPLE 1

146 parts of dimethyl 2,6-naphthalenedicarboxylate and 3.6 parts of sodium 3,5-dicarbomethoxybenzenesulfonate are mixed with 115 parts of ethylene glycol containing 0.096 part of manganous acetate and 0.056 part of antimony trioxide. The mixture is heated for 2.5 hours, during which time the temperature rises from 195° C. to about 235° C. with evolution of methanol. The pressure is then reduced to 0.07 mm. of mercury and the temperature is increased to 285° C. After 2¼ hours a polymer, polyethylene 2,6-naphthalenedicarboxylate/5-(sodium sulfo)isophthalate (98/2), is obtained having a melting point of 265° C. and a relative viscosity of 22.3 in a solvent comprising a mixture of 10 parts of phenol and 7 parts of trichlorophenol.

In similar experiments, the corresponding 96.5/3.5 copolyester is prepared as well as several control polyesters. The experiments are summarized in Table I. In each case 115 parts of ethylene glycol containing 0.096 part of manganous acetate and 0.056 part of antimony trioxide is used. The properties of the resulting polymers are listed in the table.

Each of the polyesters listed in Table I is then melted and spun into yarn, employing conventional melt-spinning apparatus. The yarns are wound up at 80 y.p.m. and drawn 3× over a hot pin heated to 150°. Tests for relative uptake with disperse dyes and for alkaline sensitivity are then carried out for each of the yarns. The results are listed in the table.

Table I

PREPARATION AND PROPERTIES OF POLYESTERS

Polyester	Starting Ester	Parts Starting Ester	Parts SDBS ³	Relative Viscosity	Polymer Melting Point, degrees	Disperse Dye Relative Uptake	Alkaline Sensitivity
1. Polyethylene 2,6-naphthalenedicarboxylate....	DM 2,6-N ¹ ...	149	none	30	265	0.5	0.3
2. Polyethylene 2,6-naphthalenedicarboxylate/5-(sodium sulfo)isophthalate (98/2).....	DM 2,6-N ¹ ...	146	3.6	22.3	255	1.2	1.6
3. Polyethylene 2,6-naphthalenedicarboxylate/5-(sodium sulfo)isophthalate (96.5/3.5).....	DM 2,6-N ¹ ...	144	6.1	32	250	2.2	2.7
4. Polyethylene terephthalate.....	DMT ²	118	none	30	255	1.0	1.0
5. Polyethylene terephthalate/5-(sodium sulfo)isophthalate (98/2).....	DMT ²	116	3.6	20	250	1.2	10.0
6. Polyethylene terephthalate/5-(sodium sulfo)isophthalate (96.5/3.5).....	DMT ²	114	6.1	20	245	1.4	27

¹ Dimethyl 2,6-naphthalenedicarboxylate.

² Dimethyl terephthalate.

³ Sodium 3,5-dicarbomethoxybenzenedisulfonate.

R may also contain as inert groups one or more additional —SO₃M groups, an example of such a compound being dipotassium 5-carbomethoxybenzene 1,3-disulfonate.

The preferred embodiment of the invention comprises a polyester in which at least about 75% of the acid component of the polyester is a naphthalenedicarboxylic acid. By "acid component" of the polyester is meant the sum of all the carboxylic acids which would be formed by

The test for relative uptake with disperse dyes is carried out by boiling one part of the test fabric for 45 minutes in 1000 parts of an aqueous mixture containing 0.4% of a mixture of equal parts of dimethyl terephthalate and benzanilide and 0.004% of 3'-hydroxyquinophthalone, a yellow disperse dye as disclosed in U.S. Patent 2,006,022. The dyed fabric is extracted with chlorobenzene and the amount of dye is estimated

spectrophotometrically from the chlorobenzene solution. The results given in Table I are based on assigning an arbitrary value of unity to the amount of dye adsorbed by the polyethylene terephthalate fabric. As indicated in the table, the fabric comprised of polyethylene naphthalenedicarboxylate containing a sulfonate salt copolymeric unit has a good level of disperse dyeability, being excellent at 3.5% copolymer level. Fabrics comprised of unmodified polyethylene naphthalenedicarboxylate have a relatively poor level of disperse dyeability, while fabrics comprised of polyethylene terephthalate containing a sulfonate salt copolymeric unit have a disperse dyeability not markedly higher than that of fabric comprised of unmodified polyethylene terephthalate.

When the fabrics comprised of the polyesters listed in Table I are treated for one hour at 100° C. with an aqueous solution of 0.4% of a mixture of equal parts of dimethyl terephthalate and benzanilide and 0.05% of Fuch-sine SBP dye, a basic dye of the triphenylmethane type, the fabrics comprised of unmodified polyethylene, terephthalate and unmodified polyethylene naphthalenedicarboxylate are essentially undyed. However, each of the fabrics comprised of a polyester containing a sulfonate salt copolymeric unit is dyed to an excellent shade of purple.

ter at 55° C., and tumbling the fabrics dry in an automatic dryer at 70° C. The fabrics are allowed to hang 1.5 hours and are then evaluated by a group of persons on an arbitrary subjective scale using the following ratings:

- 5 represents a perfectly flat fabric
- 4 represents a fabric deviating only slightly from flat
- 3 represents a fabric acceptable for wearing without ironing
- 2 represents a fabric of borderline acceptability for wearing without ironing, easily "touched up"
- 1 represents a fabric unacceptably wrinkled for wearing without ironing, although readily ironed
- 0 represents a wrinkled fabric for which considerable ironing attention is required

The average ratings determined in this way are reported in Table II. As noted in the table, fabrics comprised of polyethylene naphthalenedicarboxylate modified with copolymeric sulfonate salt units have a wash-wear rating comparable to ratings for fabrics of unmodified polyethylene terephthalate. In contrast, fabrics comprised of polyethylene terephthalate modified with copolymeric sulfonate salt units have a poor wash-wear rating.

Table II
PERFORMANCE OF POLYESTER FABRICS

Polyester fabric	Yarn count	Weave (basket)	Wash-wear rating	Weave (taffeta)	Monsanto crease recovery, percent	
					40° C.	60° C.
1. Polyethylene 2,6-naphthalenedicarboxylate/5-(sodium sulfo)-isophthalate (97.5/2.5)	103/34	102 x 92	2.3	100 x 70	61	48
2. Polyethylene terephthalate/5-(sodium sulfo)-isophthalate (98/2)	87/34	104 x 92	0.6	102 x 72	47	34
3. Polyethylene 2,6-naphthalenedicarboxylate	104/34	102 x 80	3.5	108 x 84	69	53
4. Polyethylene terephthalate	100/34	106 x 84	2.5	106 x 82	65	41

The test for alkaline sensitivity is carried out by boiling one part of the test fabric in 1000 parts of a 1% aqueous solution of sodium hydroxide for 3 hours. The results given in Table I are based on assigning an arbitrary value of unity to the fractional weight lost by the polyethylene terephthalate fabric. As indicated in the table, modification of polyethylene terephthalate with copolymeric sulfonate salt units results in a very marked increase in the alkaline sensitivity of the fabric. In contrast, fabrics of polyethylene naphthalenedicarboxylate modified with copolymeric sulfonate salt units have a much more acceptable level of alkaline sensitivity, closer to the level observed in fabrics of unmodified polyethylene terephthalate.

EXAMPLE 2

Polyethylene 2,6-naphthalenedicarboxylate/5-(sodium sulfo)isophthalate (97.5/2.5) is prepared in accordance with the method of Example 1, using 45.4 parts of dimethyl 2,6-naphthalenedicarboxylate and 1.4 parts of sodium 3,5-dicarboxymethoxybenzenesulfonate. Polyethylene 2,6-naphthalenedicarboxylate, polyethylene terephthalate, and polyethylene terephthalate/5-(sodium sulfo)isophthalate (98/2) are also prepared as described. Each of the polyesters is then melted and spun into yarn, employing conventional melt-spinning apparatus. The yarns are wound up at 1200 y.p.m. and drawn 2X over a 175° hot plate.

Basket weave and taffeta fabrics are then prepared from the drawn yarns, and the resulting fabrics are evaluated for wash performance and crease recovery in a series of tests for which the results are given in Table II.

The wash-wear rating of the fabrics is carried out by washing the fabrics in a home model washing machine using water at 55° C. with a commercially available detergent for home laundry use, rinsing the fabric in wa-

Monsanto crease recovery values are determined in accordance with Tentative Test Method 66-1959 in the Technical Manual of the American Association of Textile Chemists and Colorists, volume XXXV, Howes Publishing Co., New York city (1959), pages 171-3. The fabrics are creased while wet with 40° C. water in one series of tests and with 60° C. water in a second series of tests. The results for each series of tests, calculated as percent recovery from a standard crease in 120 seconds, are reported in Table II. As indicated in the table, fabrics comprised of polyethylene naphthalenedicarboxylate modified with copolymeric sulfonate salt units have 40° C. crease recovery values comparable to values for fabrics of unmodified polyethylene terephthalate, and 60° C. crease values superior to values for fabrics of unmodified polyethylene terephthalate. By contrast, fabrics comprised of polyethylene terephthalate modified with copolymeric sulfonate salt units have relatively poor crease recovery values.

EXAMPLE 3

146 parts of dimethyl 1,4-naphthalenedicarboxylate and 6.4 parts of sodium 3,5-dicarboxymethoxybenzenesulfonate is mixed with 260 parts of a 70% solution of p-hexahydroxyethylene glycol (70% trans, 30% cis-) in methanol. Five parts of an 8% solution of (n-C₄H₉O)₆TiHNa in butanol is added and the mixture heated for one hour at 215° C. Methanol is removed by a stream of nitrogen. The temperature is increased to 295° C. and the glycol is removed by vacuum distillation at 0.1 mm. for 1.5 hours. After cooling, the polymer is crushed and the viscosity is increased by solid phase polymerization at 250° C. under vacuum for 3.5 hours. The relative viscosity is 21.5 and the polymer melt temperature is 275° C. Yarn is spun from the polymer and drawn, after which a fabric is prepared which exhibits good wash-wear performance. One

part by weight of the fabric is immersed for 90 minutes at the boil in 1000 parts of an aqueous solution of 0.5% of o-phenylphenol and 0.03% of Brilliant Green dye (Color Index No. 42040), a basic dye of the triphenylmethane type, whereupon the fabric is dyed a deep shade of green with good wash-fastness properties. Another sample of the fabric is dyed an attractive shade of yellow with 3'-hydroxyquinophthalone under the dye-bath conditions described in Example I.

Similar results are obtained by repeating the above experiment, substituting 2.2 parts of potassium 2,5-dicarbomethoxybenzenesulfonate for the sodium 3,5-dicarbomethoxybenzenesulfonate. The experiment is repeated again, substituting 4.5 parts of sodium 3-hydroxypropane-1-sulfonate for the sodium 3,5-dicarbomethoxybenzenesulfonate, whereupon similar results are obtained.

EXAMPLE 4

131 parts of dimethyl 1,5-naphthalenedicarboxylate and 5.7 parts of sodium 3,5-dicarbomethoxybenzenesulfonate are mixed with 160 parts of p-hexahydroxylylene glycol (50% cis-, 50% trans-). Four parts of an 8% solution of $(n-C_4H_9O)_6TiHNa$ in butanol are added and the mixture is heated at 215° C. for 0.75 hour. Methanol is removed in a stream of nitrogen. The temperature is increased to 285° and glycol is removed by distillation at 0.05 mm. for 2.5 hours. The polymer is crushed and the relative viscosity is increased to 23 by solid phase polymerization under vacuum at 250° C. for 5 hours. The polymer melts at 270° C. and yields fibers which are strong and resilient after drawing. Fabrics prepared from the fibers exhibit good wash-wear performance and are readily dyed by Brilliant Green dye and by 3'-hydroxyquinophthalone under the conditions described in Examples 3 and 1, respectively.

Similar results are obtained by repeating the above experiment, substituting 4.5 parts of sodium m-carbomethoxybenzenesulfonate for the sodium 3,5-dicarbomethoxybenzenesulfonate.

EXAMPLE 5

146 parts of dimethyl 2,6-naphthalenedicarboxylate and 6.4 parts of sodium 3,5-dicarbomethoxybenzenesulfonate are mixed with 180 parts of p-hexahydroxylylene glycol (50% cis-, 50% trans-) and 5 parts of an 8% solution of $(n-C_4H_9O)_6TiHNa$ in butanol. The mixture is heated at 210-230° C. for 0.5 hour with evolution of methanol. The temperature is increased to 290° C. and the pressure is reduced to 0.07 mm. Glycol is removed by vacuum distillation at 295° C. for 1.5 hours. The polymer has a relative viscosity of 30.5 and melts at 260° C. It is readily spun into fibers which are strong and resilient after drawing. Fabrics prepared from the fibers exhibit good wash-wear performance and are readily dyed by Brilliant Green dye and by 3'-hydroxyquinophthalone under the conditions described in Examples 3 and 1, respectively.

Similar results are obtained by repeating the above experiment, substituting 6.4 parts of sodium 4,4-dicarbomethoxy-1-butanedisulfonate for the sodium 3,5-dicarbomethoxybenzenesulfonate.

EXAMPLE 6

146 parts of dimethyl 2,7-naphthalenedicarboxylate and 6.4 parts of sodium 3,5-dicarbomethoxybenzenesulfonate are mixed with 180 parts of trans-p-hexahydroxylylene glycol and 5 parts of an 8% solution of $(n-C_4H_9O)_6TiHNa$ in butanol. The mixture is heated for one hour at 215-225° C. with evolution of methanol. The temperature is increased to 285° C. and the pressure is reduced to 0.05 mm. Glycol is removed by vacuum distillation at 285° C. for 2.5 hours. The polymer is crushed and the relative viscosity is increased to 27 by solid phase polymerization under vacuum at 240° C. for 4 hours. The polymer melts at 260° C. and yields fibers which are strong and resilient after drawing. Fabrics prepared from the fibers exhibit good wash-wear performance and are readily dyed by Brilliant Green dye and by 3'-hydroxyquinophthalone under the conditions described in Examples 3 and 1, respectively.

Similar results are obtained by repeating the above experiment, substituting 115 parts of ethylene glycol for the p-hexahydroxylylene glycol.

It will be apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore it is not intended to be limited except as indicated in the appended claims.

I claim:

1. A fabric comprised of fibers of a polymeric synthetic linear fiber-forming condensation copolyester of (1) a naphthalenedicarboxylic acid; (2) a glycol selected from the class consisting of ethylene glycol, p-hexahydroxylylene glycol, and their ester-forming derivatives; and (3) from 1% to 5% thereof of a compound having the formula X_nRSO_3M in which X is a group selected from the class consisting of carboxyl, hydroxyl and ester-forming derivatives thereof; n is an integer from 1 to 2; R is a group selected from the class consisting of hydrocarbons, halogen substituted hydrocarbons and chalcogen substituted hydrocarbons; said hydrocarbon group being free from aliphatic unsaturation; and M is a metal.

2. The fabric of claim 1 in which at least 75% of the acid component of the polyester is a β,β' -naphthalenedicarboxylic acid.

3. The fabric of claim 2 in which the naphthalenedicarboxylic acid is 2,6-naphthalenedicarboxylic acid.

4. The fabric of claim 2 in which the naphthalenedicarboxylic acid is 2,7-naphthalenedicarboxylic acid.

5. A wash-wear fabric of claim 1 having a wash-wear rating as herein described of greater than 2.

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Disclaimer

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Hereby enters this disclaimer to claims 1 and 5 of said patent.
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