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TEXTILE FIBER COMPRISING AN ADMIXTURE OF A POLYESTER AND AN ADDITION POLYMER HAVING A TRIBROMONEOPENTYL GROUP IN THE REPEATING UNIT OF THE ADDITION POLYMER

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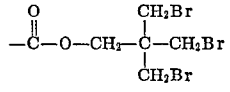
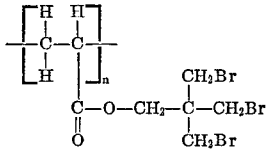
ABSTRACT OF THE DISCLOSURE

Disclosed are flame retardant textile fibers comprising an admixture of a polyester and an addition polymer having the



group as a portion of the polymer unit. The polyester is derived from at least 90 mole percent terephthalic acid and at least 90 mole percent ethylene glycol, tetramethylene glycol, or 1,4-cyclohexanedimethanol. The addition polymer preferably comprises at least 95 mole percent units of the structure



The texile fibers of this invention are flame retardant and exhibit a desirable and unobvious combination of other properties necessary in a commercially acceptable textile fiber.

This invention relates to a flame retardant textile fiber exhibiting a combination of properties necessary in a commercially acceptable textile fiber.

The use of synthetic textile fibers has increased tremendously over the last several decades. This increased use has resulted in large part from the desirable combination of properties that can be achieved in a textile article by using synthetic fibers or blends of natural and synthetic fibers. Although a synthetic textile fiber may have any number of desirable properties, every textile fiber must have a number of necessary properties to make the fiber commercially acceptable for typical applications such as wearing apparel, carpets and the like. Historically, the necessary properties include desirable mechanical properties, lack of discoloration during and immediately after spinning, light-fastness of the undyed fibers, desirable dye takeup, light-fastness of the dyed fibers and retention of dye after dry cleaning and washing.

One undesirable property of most synthetic fibers is the lack of flame retardancy. The growing significance of this property has now caused many textile fibers to be regarded as commercially unsatisfactory for many applications because of the lack of flame retardancy even though the textile fibers exhibit all the properties historically necessary for commercial acceptance. One particular and significant instance where textile fibers must be flame retardant is the children's sleepwear field where polyester cotton blends enjoy popularity.

Therefore, to meet current standards for many typical applications, including particularly children's sleepwear, the properties that have been historically necessary for

commercially acceptable textile fibers must be revised to include at least moderate flame retardancy and in some cases substantial flame retardancy.

Efforts to produce synthetic fibers which will meet many of the current standards of flame retardancy and still exhibit other properties necessary for commercial acceptance have generally been unsatisfactory. The failure to produce the desired fiber has not generally resulted from an inability to impart flame retardancy to a fiber but instead has resulted from an inability of the fiber to retain the flame retardancy after dry cleaning or laundering or from an inability to impart flame retardancy and still retain the combination of other properties which have been historically necessary in commercially acceptable fibers. Specifically, it is well known in the art that compounds containing bromine and/or chlorine of virtually every kind and description, and particularly brominated aromatic compounds, are all effective in imparting flame retardancy to polyester fibers; however, the compounds typically either wash or dry clean out and destroy the flame retardancy of the fiber or result in one or more of of the commercially necessary properties being unsatisfactory. For example, the addition of bromine-containing compounds to polyester fibers often results in unsatisfactory mechanical properties, discoloration of the fiber during and immediately after melt spinning, unsatisfactory light-fastness of the undyed fiber and unsatisfactory light-fastness of the dyed fibers. Also the bromine containing compounds often wash or dry clean out to produce a level of flame retardancy substantially the same as a polyester fiber not containing a bromine-containing compound.

We have now discovered a textile fiber that retains a high degree of flame retardancy after dry cleaning and washing and in addition exhibits a combination of other necessary properties to make the fiber commercially acceptable. Thus, we have at last discovered a textile fiber that exhibits not only the historically necessary properties for commercial acceptability, but exhibits a high degree of flame retardancy after washing and dry cleaning.

Accordingly, an advantage of the textile fiber of this invention is the high degree of flame retardancy after washing and dry cleaning.

Another advantage of the textile fiber of this invention is the desirable mechanical properties.

Another advantage of the textile fiber of this invention is the lack of substantial discoloration of the fibers during and immediately after melt spinning.

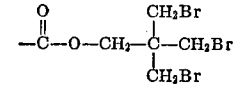
Still another advantage of the textile fiber of this invention is the desirable dye takeup.

Yet another advantage of the textile fiber of this invention is the desirable light-fastness of the dyed fiber.

Yet another advantage of the textile fiber of this invention is the retention of dye after dry cleaning and washing.

Other advantages and features of this invention will be readily apparent to those skilled in the art from the following description and appended claims.

We have accomplished the remarkable objective of obtaining a flame retardant textile fiber that exhibits a desirable combination of properties necessary for commercial acceptance by discovering a textile fiber broadly comprising an admixture of a polyester and an addition polymer having the



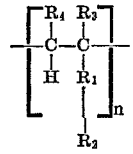
group as a portion of the polymer unit.

More specifically, the textile fiber of this invention comprises an admixture of

(A) a fiber forming polyester derived from
  (1) a dicarboxylic acid which is at least 90 mole percent terephthalic acid, and
  (2) a diol which is at least 90 mole percent ethylene glycol, tetramethylene glycol, or 1,4-cyclohexanedimethanol, and
(B) a sufficient quantity to comprise 0.1–10 weight percent bromine, based on the combined weight of (A) and (B), of an addition polymer comprised of units having the above noted group in the polymer unit.

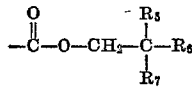
Broadly, the fiber forming polyester can be derived from a dicarboxylic acid which is at least 90 mole percent terephthalic acid, and a diol which is at least 90 mole percent ethylene glycol, tetramethylene glycol, or 1,4-cyclohexanedimethanol. The remaining dicarboxylic acid can be aliphatic, alicyclic, and aromatic dicarboxylic acids having up to 40 carbon atoms. Examples of such acids include malonic, succinic, adipic, azelaic, sebacic, suberic, 1,4-cyclohexenedicarboxylic, and isophthalic. The remaining dicarboxylic acid can contain substituents that impart basic or acid dyeability to the fiber. The remaining diol can be aliphatic, alicyclic, or aromatic and can have up to 40 carbon atoms. Examples of such diols include diethylene glycol, 1,2-propylene glycol, 1,3-cyclohexanedimethanol and hydroquinone. The remaining diol can contain substituents that impart basic or acid dyeability to the fiber. In one specific embodiment the polyester can be derived from terephthalic acid and ethylene glycol. The polyesters of this invention have an inherent viscosity of at least 0.4 measured at 25° C. using 0.23 gram of polymer per 100 ml. of a solvent composed of 60 volumes of phenol and 40 volumes of tetrachloroethane.

Broadly, the addition polymer can be comprised of units corresponding to the structure



wherein

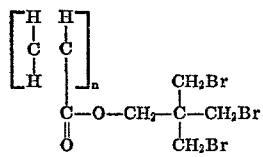
R_1 is a covalent bond or a $—CH_2—$group,
R_2 is a radical corresponding to the structure



R_3 is —H or a monovalent alkyl radical containing 1–8 carbon atoms, or R_2
wherein R_5, R_6 and R_7 are $—CH_2Br$, $—CHBr_2$ or $—CBr_3$, and R_4 is —H or R_2.

In one embodiment R_1 above can be a covalent bond. In another embodiment where R_1 is a covalent bond, R_3 can be —H or $—CH_3$.

In still one further embodiment R_1 can be a covalent bond, R_3 can be —H or $—CH_3$ and R_4 is —H and R_5, R_6 and R_7 can be $—CH_2Br$. In this embodiment the addition polymer can be comprised of polymer units formed from tribromoneopentyl acrylate and these polymer units have the structure

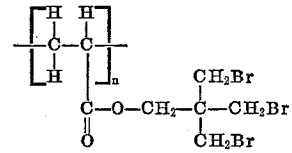


The addition polymers of this invention are well known in the art and are disclosed in references such as U.S. 3,165,502.

Broadly the amount of addition polymer can be a sufficient quantity to comprise 0.1–10 weight percent bromine, based on the combined weight of polyester and addition polymer. More specifically the amount of addition polymer can comprise 2–8 weight percent, based on the weight of polyester and addition polymer.

Broadly, the addition polymer can contain, even in major quantities, repeating units other than repeating units disclosed above. More specifically, the addition polymer can be a copolymer containing the above-disclosed repeating units and other addition polymer units derived from vinyl and isopropenyl esters of monobasic saturated fatty acids containing from 2–18 carbon atoms, e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl stearate, etc., and corresponding isopropenyl esters, alkyl vinyl ethers wherein the alkyl group contain from 1–4 carbon atoms, e.g., methyl vinyl ether, ethyl vinyl ether, etc., alkyl vinyl ketones wherein the alkyl group contains from 1–4 carbon atoms, e.g., methyl vinyl ketone, etc., vinyl derivatives of benzene, e.g., styrene, α-methylstyrene, etc. vinyl and vinylidene halides, e.g., vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, etc., tetrafluoroethylene, chlorotrifluoroethylene, α-olefins containing from 2–8 carbon atoms, e.g., ethylene, isobutylene, etc., and monoalkyl and dialkyl esters of α,β-unsaturated dicarboxylic acids wherein, the alkyl groups contains from 1–4 carbon atoms, e.g., monomethyl maleate, monobutyl maleate, dimethyl maleate, dibutyl maleate, etc., and corresponding esters of fumaric, itaconic, and the like.

In one embodiment the addition polymer comprises at least 35 mole percent, and in another embodiment at least 95 mole percent, units of the structure



As noted above, one desirable characteristic of the textile fibers of this invention is their mechanical properties. More specifically, the mechanical properties of the textile fibers of this invention, such as tenacity, elongation and modulus, are quite similar to a control fiber not containing the addition polymer. In one embodiment the tenacity is less than 35% lower, the elongation is less than 15% lower and the modulus is less than 10% lower than a control fiber containing no addition polymer.

Another desirable characteristic of the textile fibers of this invention is the lack of substantial discoloration during and immediately after being melt spun as compared to a control fiber having other types of bromine containing molecules thereon. As is well known in the art, many types of bromine containing molecules cause the fiber to yellow during and after melt spinning.

Still another desirable characteristic of the textile fibers of this invention is the very desirable light-fastness of the undyed fibers. Specifically, no yellowing or other discoloration is observed after 80 hours exposure to a carbon-arc Fade-Ometer. A control textile fiber containing other bromine containing molecules can in many instances exhibit significant yellowing after exposure to a Fade-Ometer.

One additional characteristic of the textile fibers of this invention is desirable dye takeup. Dye takeup is an essential requirement for a commercial fiber. The textile fibers of this invention dye to deep shades and exhibit commercially acceptable dye takeup levels. A control textile fiber containing many other kinds of bromine-containing compounds does not dye to deep shades.

Yet another desirable characteristic of the textile fibers of this invention is the light-fastness of the dyed fibers. No fading of the textile fibers of this invention is observed after 20 hours and in some cases after 80 hours in a carbon-arc Fade-Ometer. A control textile fiber which

contains other bromine-containing compounds can in many instances exhibit significant fading in a similar test.

One further desirable characteristic of the fibers of this invention is the retention of dye after dry cleaning and washing. Textile fibers containing many other kinds of bromine-containing molecules do not retain a satisfactory level of dye after dry cleaning and washing.

The textile fibers of this invention exhibit desirable retention of flame retardancy after washing and dry cleaning because the bromine does not wash or dry clean out of the textile fibers of this invention. In one embodiment the textile fibers of this invention retain at least 90 weight percent bromine, and in some cases at least 95 weight percent bromine, based on the weight of the bromine before washing, after 10 washings in accordance with AATCC Test Method 61–1969, Number III–A. In one embodiment the textile fibers of this invention retain, based on the weight of bromine before dry cleaning, at least 90 weight percent bromine, and in some cases at least 95 weight percent bromine, after 15 dry cleanings in accordance with AATCC Test Method 132–1969.

After washing and dry cleaning the textile fibers of this invention exhibit an Oxygen Index of greater than 21 and in many cases greater than 23. In one embodiment the textile fibers of this invention pass the so called Children's Sleepwear test (FR Doc. 71–10837).

The polymers of this invention can be formed according to conventional well known polymerization techniques. The polyesters of this invention can be formed by direct condensation, ester interchange, or acidolysis. The addition polymers of this invention can be formed by solution, bulk, emulsion or bead polymerization. The monomers from which the addition polymer units are derived can be prepared using materials and procedures well known in the art such as the reaction of tribromoneopentyl alcohol and the corresponding carboxylic acid anhydride such as described in U.S. 3,165,502.

The admixture of the polyester and the addition polymer can be accomplished by procedures well known in the art such as physically mixing small particles of the materials, co-extrusion, or slurrying a solution of the additive with polyester powder and evaporating off the solvent.

These admixtures of the polyester and the addition polymer can be spun by conventional spinning techniques such as melt spinning.

The following examples are presented to illustrate the invention and are not to be interpreted as limiting the invention to the specific embodiments of the examples.

EXAMPLE 1

This example describes the preparation of textile fibers of poly(ethylene terephthalate) and poly[3-bromo-2,2-bis(bromomethyl) propyl acrylate] often called poly(tribromoneopentyl acrylate).

In an evaporating dish is placed 184.2 g. of poly(ethylene terephthalate) powder having an inherent viscosity of 0.60. To the dish is added a solution of 15.8 g. poly[3-bromo-2,2-bis(bromomethyl)propyl acrylate] (I.V.= 0.07) in 150 ml. methylene chloride. The solvent is evaporated off at 40° C. with stirring while in a hood. Final drying is performed at 50° C. and 0.1 mm. to give an intimate mixture of poly(ethylene terephthalate) containing 7.9% poly[3-bromo-2,2-bis(bromomethyl) propyl acrylate]. This mixture is melt spun at 275° C. to produce nondiscolored fibers having an inherent viscosity of 0.56. The fibers are drawn in water at 68° C. and then in superheated steam for an overall draw factor of 4.0. After being heatset in a relaxed state for 5 min. at 145° C., the fibers are not discolored and have the following properties: 3.0 den./fil., 3.9 g./den. tenacity, 26% elongation and 42 g./den. elastic modulus. A tube knitted from these fibers showed no yellowing after 80 hr. exposure in a carbon-arc Fade-Ometer. On another sample of the tube the Chlidren's Sleepwear Test (FR Doc. 71–10837) is carried out. The fibers pass the test. The Limiting Oxygen Index is 23.1. On another knitted sample, 15 dry cleaning cycles with perchloroethylene are carried out according to AATCC Test Method 132–1969. Bromine analyses before and after the test indicate no loss of bromine. These fibers dye to deep shades and retain the dye during washing and dry cleaning.

Similar results are achieved when poly(tetramethylene terephthalate) or poly(1,4-cyclohexylenedimethylene terephthalate) are used in place of poly(ethylene terephthalate).

EXAMPLE 2

This example describes the preparation of textile fibers of poly(ethylene terephthalate) and an addition polymer having 50 mole percent bromine containing units.

A mixture of 50 mole percent tribromoneopentyl fumarate and 50 mole percent styrene is polymerized in cyclohexanone solution, is isolated as the powder by precipitation in methanol, and is blended in poly(ethylene terephthalate) to give a 92/8 wt. percent polyester/addition polymer blend. This composition is melt spun to give a fiber having the following properties:

Denier	1.28
Tenacity, g./den.	4.77
Elongation, percent	20
Elastic modulus, g./den.	60

The fibers are not discolored after melt spinning and the undyed fibers have excellent light-fastness. The fibers dye to deep shades and retain the dye during washing and dry cleaning. The fibers retain at least 90% bromine after 10 washings in accordance with AATCC Test Method 61–1969, Number III–A and 15 dry cleaning cycles in accordance with AATCC Test Method 132–1969. The fibers pass the Children's Sleepwear Test (FR Doc. 71–10837).

Similar results are achieved when poly(tetramethylene terephthalate) or poly(1,4-cyclohexylenedimethylene terephthalate) are used in place of poly(ethylene terephthalate).

EXAMPLE 3

Table I below illustrates several textile fibers of poly(ethylene terephthalate) and various addition co-polymers. Properties of these fibers are similar to those obtained in Examples 1 and 2.

TABLE I

Fiber No.	Comonomer 1	Comonomer	Molar ratio of comonomers in copolymer	Weight ratio of poly(ethylene terephthalate)ed copolymer
1	Tribromoneopentyl acrylate	Methyl acrylate	75/25	90/10
2	Tribromoneopentyl methacrylate	Ethyl methacrylate	60/40	90/10
3	Tribromoneopentyl fumarate	Vinyl acetate	50/50	92/8
4	Tribromoneopentyl maleate	Vinyl ethyl ether	50/50	90/10
5	Tribromoneopentyl itaconate	Ethylene	40/60	80/20
6	Tribromoneopentyl acrylate	Vinyl methyl ketone	85/15	85/15
7	Tribromoneopentyl fumarate	Vinylidine fluoride	50/50	95/5

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modification can be effected within the spirit and scope of the invention.

We claim:

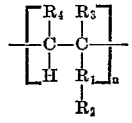
1. A textile fiber comprising an admixture of

(A) a fiber forming polyester having an inherent viscosity of at least 0.4 measured at 25° C. using 0.23 gram of polymer per 100 ml. of a solvent composed of 60 volumes of phenol and 40 volumes tetrachloroethane, the polyester being derived from

(1) a dicarboxylic acid which is at least 90 mole percent terephthalic acid, and

(2) a diol which is at least 90 mole percent ethylene glycol, tetramethylene glycol, or 1,4-cyclohexanedimethanol, and

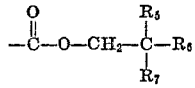
(B) a sufficient quantity to comprise 0.1–10 weight percent bromine, based on the combined weight of (A) and (B), of an addition polymer comprised of units corresponding to the structure



wherein

R_1 is a covalent bond or a $—CH_2—$ group,

R_2 is a radical corresponding to the structure



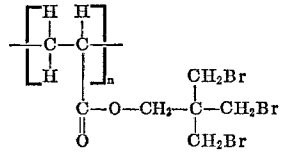
R_3 is —H or a monovalent alkyl radical containing 1–8 carbon atoms, or R_2 wherein R_5, R_6 and R_7 are $—CH_2Br$, $—CHBr_2$ or $—CBr_3$, and R_4 is —H or R_2.

2. The fiber of claim 1 wherein the fiber forming polyester is derived from terephthalic acid and ethylene glycol, and R_1 is a covalent bond.

3. The fiber of claim 2 wherein R_3 is —H or $—CH_3$.

4. The fiber of claim 3 wherein R_4 is —H, and R_5, R_6 and R_7 are $—CH_2Br$.

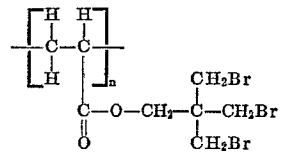
5. The fiber of claim 4 wherein the addition polymer comprises at least 35 mole percent units of the structure



6. A textile fiber comprising an admixture of

(A) a fiber forming polyester having an inherent viscosity of at least 0.4 measured at 25° C. using 0.23 gram of polymer per 100 ml. of a solvent composed of 60 volumes of phenol and 40 volumes tetrachloroethane, the polyester being derived from terephthalic acid and ethylene glycol,

(B) based on the combined weight of (A) and (B), from 2–8 weight percent of an addition polymer having at least 95 mole percent units of the structure



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