FLAME AND HEAT RESISTANT STRETCH FABRICS WITH IMPROVED CHEMICAL RESISTANCE AND DURABILITY

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ABSTRACT

The present invention relates to flame and heat resistant stretch fabrics with improved durability. The stretch fabrics comprise crosslinked polyolefin elastic fibers which may be combined into a core spun yarn with inherently flame resistant fibers. The elastic fibers or yarns can be conveniently formed into fabrics using well-known techniques such as, for example, warp or weft weaving or by using co-knitting techniques with other flame resistant fibers or yarns. Such fabrics are useful in various durable or repeated-use fabric applications such as, but not limited to, clothing (in particular protective garments), and upholstery.
FLAME AND HEAT RESISTANT STRETCH FABRICS WITH IMPROVED CHEMICAL RESISTANCE AND DURABILITY

BACKGROUND AND SUMMARY OF THE INVENTION

[0001] The present invention relates to flame and heat resistant stretch fabrics with improved durability. The stretch fabrics comprise crosslinked polyolefin elastic fibers which may be combined into a core yarn with inherently flame resistant fibers. The elastic fibers or yarns can be conveniently converted into fabrics using well-known techniques such as, for example, weaving or by using co-knitting techniques with other flame resistant fibers or yarns. Such fabrics are useful in various durable or repeated-use fabric applications such as, but not limited to, clothing (in particular protective garments), and upholstery.

[0002] Workers whose occupations put them at risk of exposure to heat and/or flame, such as foundry workers and workers the chemical and refinery industries, wear protective garments to minimize the potential of serious burns or other bodily injury. In attempting to provide maximum protection against heat and fire for these workers, the emphasis in the prior art has been on using thermal and/or flame resistant fabrics to form protective garments. The flame resistant fabrics used for such garments typically are formed of woven inherently flame resistant yarns which tend to be heavy and stiff. Thus, the garments formed therefrom tend to be heavy, bulky and somewhat inflexible. The stiffness and general inflexibility of such fabrics tends to restrict the movement of a worker while wearing garments made from such fabrics.

[0003] Attempts have been made in the prior art to develop garments, that protect against exposure to extreme heat and fire, but that are flexible so as to enable greater freedom of movement to the wearer. One approach has been to use conventional, heavy, somewhat inflexible flame resistant fabrics for the majority of the garment, with portions of the garments being formed with lighter, less flame and thermally resistant materials for the joints of the garments. For example, U.S. Pat. No. 4,922,552 discloses a firefighters’ garment formed from layers of a thick, flame resistant fabric in which an outer layer of the protective flame resistant material has portions cut-away therefrom, and replaced with a layer of a lighter material having a significantly less degree of flame resistance and protective properties, but which has greater flexibility and less bulk. The problem with such a garment is that the flexibility of the garment is limited to specific portions of the garment and some flame resistance protection is sacrificed to achieve this enhanced flexibility.

[0004] More recently, U.S. Pat. No. 5,527,597 touted the use of an elastic fiber such as spandex or rubber to make protective garments more flexible. This reference teaches that since the elastic core yarns have a low resistance to heat and/or fire, that they need to be wrapped with a protective yarn such as fibers made from an aromatic polyamide/polybenzimidazole (PBI) blend. The wrap fibers were designed to protect the elastic core yarns from direct exposure to heat and fire which would otherwise cause the core yarns to degrade or melt. However, the reference acknowledged that the protective wrap would not completely protect the elastic fiber (particularly when stretched), and that breaks in the elastic yarn would eventually occur. This is particularly true when the garment is subjected to relatively long exposures to elevated temperatures, such as during industrial laundering of the garment.

[0005] Another approach to making fabrics flame resistance involves chemically treating fabrics which would otherwise not be flame resistant. Fabrics of inherently flame resistant fibers are generally considered to provide longer lasting protection, while chemically-treated fabrics (such as flame resistant cotton) are often considered to provide less lasting protection but with more comfort to the wearer. Moreover the chemical treatments used in such processes are typically too harsh for elastic fibers to survive, leading to a rapid loss of elasticity or even breaks.

[0006] Accordingly, there is still a need for a more comfortable elastic heat and/or flame-resistant fabric which is durable upon repeated exposures to industrial laundering. The present invention relates to such fabric. The fabric is elastic, flame and/or heat-resistant and durable, making it particularly well-suited for these applications.

[0007] A material is typically characterized as elastic if it has a high percent elastic recovery (that is, a low percent permanent set) after application of a biasing force. Ideally, elastic materials are characterized by a combination of three important properties, that is, (i) a low percent permanent set, (ii) a low stress or load at strain, and (iii) a low percent stress or load relaxation. In other words, there should be (i) a low stress or load requirement to stretch the material, (ii) no or low relaxing of the stress or unloading once the material is stretched, and (iii) complete or high recovery to original dimensions after the stretching, biasing or straining is discontinued.

[0008] To be used in the elastic, durable, flame and/or heat resistant fabrics of the present invention, the fibers making up the fabric should be, inter alia, stable during dyeing and heat setting processes as well as industrial laundering conditions. For an elastic polyolefin fiber to be stable under dyeing and heat-setting conditions, it must be crosslinked. These fibers can be crosslinked by one or more of a number of different methods, for example, e-beam or UV irradiation, silane or azide treatment, peroxide, etc., some methods better than others for fibers of a particular composition. For example, polyolefin fibers that are irradiated under an inert atmosphere (as opposed to irradiated under air) tend to be highly stable during dyeing processes (that is, the fibers do not melt or fuse together). The addition of a mixture of hindered phenol and hindered amine stabilizers further stabilized such fibers at higher temperatures, such as those encountered during some heat setting procedures (for example, 200-210° C. for polyethylene terephthalate (PET) fiber).

[0009] Spandex (also known as elastane), a segmented polyurethane elastic material is currently used in various stretch fabrics, including flame and heat-resistant fabrics (see U.S. Pat. No. 5,527,597). Spandex, however, is not stable at the typical high heat-setting temperatures used with some companion fibers, and moreover, spandex fabrics tend to lose their integrity, shape and elastic properties when subjected to elevated service temperatures such as those encountered in washing, drying and ironing.

[0010] It has been discovered that elastic flame and/or heat-resistant fabrics can be formed which are capable of surviving exposures that other flame and/or heat resistant fabrics do not survive. Particularly the fabrics of the present invention are durable, meaning the fabrics can survive c) 50 cycles of industrial laundering at temperatures of at least 65° C.,
wherein “surviving” means that the fabric after treatment exhibits growth of less than about 20 percent, preferably less than 10 percent, and more preferably less than about 8 percent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] The following terms shall have the indicated meaning when used in the present patent application: [0012] “Fiber” means a material in which the length to diameter ratio is greater than about 10. Fiber is typically classified according to its diameter. Filament fiber is generally defined as having an individual fiber diameter greater than about 15 denier, usually greater than about 30 denier. Fine denier fiber generally refers to a fiber having a diameter less than about 15 denier. Microdenier fiber is generally defined as fiber having a diameter less than about 100 microns denier. “Filament fiber” or “monofilament fiber” means a single, continuous strand of material of indefinite (that is, not predetermined) length, as opposed to a “staple fiber” which is a discontinuous strand of material of definite length (that is, a strand which has been cut or otherwise divided into segments of a predetermined length).

[0013] The term “flame resistant” when used in reference to the fabric or article means that the fabric or article exhibits 1) response to flame propagation, upon direct exposure to flame, graded as A grade as per DIN EN 513:02.95 standard norm (DIN ISO15025:02.03 standard testing method); 2) heat transmission on exposure to flame performances graded as B1 grade or higher (B2,B3, B4 or B5) as per DIN EN 513: 02.95 standard norm (DIN EN 667:11.92 standard testing method); 3) heat transmission on exposure to radiant heat graded as C1 or higher (C2, C3, or C4), as per DIN EN 513:02.95 standard norm (DIN EN 667:05.03 standard testing method). Fabrics or articles that can meet or exceed those requirements are considered suitable for at least “Low risk level: localized exposure to heat and/ or flame” protective clothing as per ISO 2801:1998 International Standard “Clothing for protection against heat and flame—General recommendation for selection, care and use of protective clothing”.

[0014] The term “durable” when used in reference to the fabric or article means that the fabric or article exhibits growth of less than 20 percent, preferably less than about 10 percent and more preferably less than about 8 percent, 6 percent or even 5 percent in both the warp and weft direction after 50 cycles of industrial laundering at temperatures of at least 65°C, alternatively at least 75°C, 85°C, or even 95°C.

[0015] The term “growth” means residual elongation, or the amount the fabric lengthens after applying a load over a given length of time and allowing recovery, expressed as a percentage of the initial fabric dimension. Growth can be determined using ASTM D3107.

[0016] An “elastic fiber” is one that will recover at least about 50 percent, more preferably at least 60 percent even more preferably 70 percent of its stretched length after the first pull and after the fourth to 100 percent strain (double the length). One suitable way to do this test is based on the one found in the International Bureau for Standardization of Man-made Fibers, BHSFA 1998, chapter 7, option A. Under such a test, the fiber is placed between grips set 4 inches apart, the grips are then pulled apart at a rate of about 20 inches per minute to a distance of eight inches and then allowed to immediately recover. It is preferred that the elastic textile articles of the present invention have a high percent elastic recovery (that is, a low percent permanent set) after application of a biasing force. Ideally, elastic materials are characterized by a combination of three important properties, that is, (i) a low stress or load at strain; (ii) a low percent stress or load relaxation, and (iii) a low percent permanent set. In other words, there should be (i) a low stress or load requirement to stretch the material, (ii) zero or low relaxing of the stress or unloading once the material is stretched, and (iii) complete or high recovery to original dimensions after the stretching, biasing or straining is discontinued.

[0017] “Elastic materials” are also referred to in the art as “elastomers” and “elastomeric”. For purposes of this invention, an “elastic article” is one that comprises elastic fiber.

[0018] “Nonelastic material” means a material, for example, a fiber, that is not elastic as defined above.

[0019] “Core spun yarn” means a yarn which has been made by twisting fibers around a core which is another filament or a previously spun yarn, thus at least partially concealing the core.

[0020] One aspect of this invention is an elastic, durable, flame and/or heat resistant article such as fabric or an assembled garment that comprises a heat-resistant, crosslinked elastic fiber. The fabric may be made flame and/or heat resistant by the incorporation on inherently flame resistant materials and/or the article may be subjected to a chemical treatment to impart the heat and/or flame resistance.

[0021] In one embodiment, the article is a durable stretch fabric made and processed from one or more crosslinked, heat-resistant olefin elastic fibers. The fabrics can be made by any process, for example, weaving, knitting, etc., and may use a combination of elastic and inelastic (“hard”) fibers. These fabrics exhibit excellent chemical, for example, chlorine, resistance and durability, for example, they retain their shape and feel (“hard”) over repeated exposure to service conditions, for example, washing, drying, etc. The fabric or assembled garment will exhibit a change in elasticity no greater than about 10 percent and will retain no more than about 50 percent of its growth more preferably no more than about 20 percent of its growth, more preferably no more than about 10 percent of its growth and most preferably no more than about 8 percent of its growth after a treatment of 50 cycles of industrial laundering at temperatures of at least 65°C.

[0022] The elastic fibers are preferably crosslinked, heat-resistant olefin elastic fibers. Such fibers include ethylene polymers, propylene polymers and fully hydrogenated styrene block copolymers (also known as catalytically modified polymers). The ethylene polymers include the homogeneously branched and the substantially linear homogeneously branched ethylene polymers as well as ethylene-styrene interpolymers. Crosslinked homogeneously branched and the substantially linear homogeneously branched ethylene polymers are most preferred.

[0023] The elastic fibers of the present invention may be of any suitable fiber diameter, for example, 15, 40, 70, 140 or even higher denier.

[0024] Suitable elastic fibers for use in the present invention are disclosed in U.S. Pat. No. 6,437,014, hereby incorporated by reference in its entirety. As described in that reference, the fibers can be formed by many processes known in the art, for example the fibers can be meltblown, spunbond, or more preferably made by the melt spinning process. Similarly, as taught in U.S. Pat. No. 6,437,014, the fibers can be made from many different materials, including ethylene-al-
pha olefin interpolymers, substantially hydrogenated block polymers, styrene butadiene styrene block polymers, styrene-ethylene/butene-styrene block polymers, ethylene styrene interpolymers, polypropylenes, polyamides, polyurethanes and combinations thereof. The crosslinked homogeneously branched ethylene polymers described in that reference, particularly the substantially linear ethylene polymers, are particularly well suited for use in making articles of this invention.

[0025] These elastic fibers may be used neat or may advantageously be used as the core in a core spun yarn. Core spun yarns may be easier to process in some commercial weaving or knitting machines. Furthermore, by selecting inherently flame-resistant materials for use as the wrapping fibers in a core spun yarn, the overall flame and/or heat resistance of the core spun yarn (and the articles which include such yarns) can be increased. Suitable fibrous materials for wrapping an elastic core include polyamides (including aramids), polymeric rayon, cellulose fibers (particularly flame resistant cellulose fibers), polyester (particularly flame resistant polyester), polyvinyl alcohol, polytetrafluoroethylene, wool (particularly flame resistant wool), polyvinyl chloride, polyetheretherketone, polyetherimide, polyolefins, polyimideimide, polybenoxazole, carbon, modacrylic acryllic, melamine, glass, polybenzimidazole (PBI) fibers, polye(phenylene sulfide) PPS fibers, polyacrylate, semicarbon, phenolic or novoloid fibers, modacrylic, chlrorofibers, FR viscose, nylon and acrylic and combinations thereof. Aramid fibers are particularly preferred for their flame resistance.

[0026] These fibers, whether neat or more preferably as the core in a core spun yarn, will preferably be used together in a weaving or knitting process with other fibers or yarns to make the fabric of the present invention. To increase the flame-resistant properties of the article, it may be advantageous to combine the elastic fiber or core spun yarn with inherently flame-resistant fibers. Suitable fibrous materials for combining with the elastic fiber or yarns include those listed above for use as the covering fiber in a core spun yarn. Aramid fibers may be particularly preferred for their inherent flame resistance. Usually the crosslinked, heat-resistant olefin elastic fibers comprise a minority of the fabric on a weight basis, but the exact percentage of each of the fibers may be optimized for any particular use. In general, the fabrics will contain at least about 2 percent by weight of the elastic fiber and woven fabrics will tend to have less than about 15 percent by weight of the elastic fiber whereas knitted fabrics may have up to about 35 percent by weight of the elastic fibers, but amounts outside these ranges are possible.

[0027] It may also be desirable to include a static dissipating fiber such as metallic or carbon fibers into the fabric. Garments including such static dissipating fibers will provide additional protection for workers.

[0028] The fabric of the present invention can be made according to known fabrication methods such as weaving or knitting. It will be understood by one of ordinary skill in the art that in general, for any given fabrication process, the denser the fabric construction, the more flame resistant the fabric will be. At the same time, however, the denser the fabric the heavier the fabric will be, which may make a garment made from the fabric less comfortable.

[0029] The fabric of the present invention can be used to make garments. Examples of garments which can be advantageously made from the fabric of the present invention include uniforms, particularly uniforms which are subject to industrial laundering.

[0030] The fabrics of this invention include fabrics known to require harsh and stringent processes that utilize chemicals and conditions that would degrade most conventional stretch fabrics because these chemicals and conditions would degrade the stretch fiber component of these fabrics. The fabrics of this invention, however, comprise a stretch fiber that is particularly resistant to such degradation and as such, the fabric containing these fibers exhibits surprising durability and chemical resistance.

[0031] In another embodiment of the present invention, an elastic fabric can be chemically treated to impart flame-resistance. In such methods, the fibers or articles are treated with specific chemicals to impart flame resistance to them. Such chemicals are known in the art, and include Tetrakis-(hydroxymethyl) phosphonium salts (henceforth designated THP salts), such as THPs, are very effective for imparting flame resistance to cellulosed materials. The application of such chemicals can be accomplished by using either a THP/urea precondensate salt, which is insolubilized with gaseous ammonia, or by using a THP/polymer/dry/cure process, or both. Exemplary techniques are described in U.S. Pat. Nos. 4,494,951, 4,078,101, and 5,238,464, although any known method of imparting flame resistance may be used. Treatments to enhance thermal protective performance on wool based fabrics are also known, and based on addition of hexafluorotitanate and hexafluorozirconates to wool fiber, by exhausting onto wool at or below the boil. Such treatments are commercially as Zirpro finish from IWS.

[0032] In general the chemical treatments used to impart flame-resistance expose the fiber to a harsh environment, which would degrade most elastic fibers. However, the preferred melt spun fibers comprising crosslinked homogeneously branched ethylene polymers, resist degradation even under the harsh conditions typically seen in these processes. It is contemplated that the treatment may be applied to the fiber, the fabric or even the finished product as desired.

[0033] It is also possible to combine the techniques of creating a flame and or heat resistant durable stretch fabric, for example by chemically treating a fabric made from inherently flame and or heat resistant fibers.

[0034] The following examples are to illustrate the invention, and not to limit it. Ratios, parts and percentages are by weight unless otherwise stated.

**EXPERIMENTAL**

Fiber Descriptions:

[0035] Core spun yarn is made via the Siro Spinning process. The corespun yarn comprises 91 percent by weight of Poly(amide-imide) fibers; 1 percent by weight carbon fibers and 8 percent by weight fiber made from 140 Denier crosslinked ethylene-octene copolymer fiber available from The Dow Chemical Company as Dow XLA fiber. Poly(amide-imide) fibers and carbon fiber short (cotton like) staple length in intimate blend is spun using a conventional ring spinning frame, and can be combined during the twisting process with ethylene-octene copolymer 140 den, pre-drafted at 5.2:1 ratio (draft). The process spinning process leads to form core yarns, of average count equal to Nm 1/6, where ethylene-octene copolymer 140 den 5.2x drafted makes up the core, and of Poly(amide-imide) fibers and carbon fibers...
the outer covering sheath. Cohesion within the covering fiber is imparted by applying twist level equal to: 570 twist per meter.

[0036] A fabric is then woven using this core spun yarn as the weft component. Yarns of similar NM 1/2S count, based on 99 percent by weight Polyamide-imide fibers and 1 percent by weight carbon fiber short (cotton like) staple length are used as warp component. Loom settings are: total number of warp threads 4867, reed width 201 cm; 2550 weft picks per m.

[0037] Fabric so woven is then finished with a relaxation process in open width form to promote shrinkage in the weft direction and allow for the desired extensibility. This fabric is then tested for flame resistance as follows:

[0038] 1) response to flame propagation, upon direct exposure to flame, as per DIN EN 531:02.95 standard norm (DIN ISO15025:02.03 standard testing method): resulting grade A;

[0039] 2) heat transmission on exposure to flame as per DIN EN 531:02.95 standard norm (DIN EN 367:11.92 standard testing method): resulting grade B1;

[0040] 3) heat transmission on exposure to radiant heat, as per DIN EN 531:02.95 standard norm (DIN EN 366:05.93 standard testing method): resulting grade C1

[0041] Elasticity is tested by the method known in the art as TTM077 DuPont method (Total elongation of woven fabrics); while growth is tested by the methods known in the art as TTM077 DuPont method (Percentage of fabric growth in stretch woven). The growth and elongation on the fabric in this example are elongation 10 percent, growth after 1 min—4.0 percent; growth after 1 hour—3.2 percent.

[0042] These fabrics will exhibit similar durability as those reported in WO 03/078723 A1 (hereby incorporated by reference in its entirety), particularly those described in Example 5 “Laundering”.

[0043] Although the invention has been described in considerable detail through the preceding embodiments, this detail is for the purpose of illustration. Many variations and modifications can be made on this invention without departing from the spirit and scope of the invention as described in the following claims. All references including patents and patent applications cited above are incorporated herein by reference.

What is claimed is:

1. A process of making a durable stretch flame or heat resistant article comprising a) selecting an elastic fiber comprising a crosslinked polyolefin; and b) combining the fiber of step (a) with one or more inherently flame resistant fibers to make an article.

2. The process of claim 1 wherein the crosslinked polyolefin is a crosslinked homogeneously branched ethylene polymer.

3. The process of claim 1 wherein the crosslinked homogeneously branched ethylene polymer is used as a core in a core spun yarn prior to step (b).

4. The process of claim 3 wherein the outer covering of the core spun yarn is a fiber having inherently flame and/or heat resistant properties.

5. The process of claim 4 wherein the outer covering comprises polyamide fiber.

6. The process of claim 5 wherein the polyamide fiber is an aramid fiber.

7. The process of claim 1 wherein the inherently flame resistant fibers of step (b) comprise polyamide fibers.

8. The process of claim 1 wherein the inherently flame resistant fibers of step (b) comprise aramid fibers.

9. The process of claim 1 wherein step (b) further comprises combining a static dissipating fiber.

10. A durable elastic flame and/or heat resistant article comprising an elastic fiber comprising a crosslinked polyolefin; and inherently flame resistant fibers.

11. The article of claim 10 wherein the crosslinked polyolefin is a homogeneously branched ethylene polymer.

12. The article of claim 10 characterized in that said article will exhibit growth of less than 20 percent after 50 cycles of industrial laundering at temperatures at least about 65°C.

13. The article of claim 12 wherein the growth is less than 10 percent.

14. The article of claim 13 wherein the growth is less than 8 percent.

15. The article of claim 10 wherein the article is a woven or knitted fabric.


17. The article of claim 10 wherein the inherently flame resistant fibers comprise polyamide fibers.

18. The article of claim 10 further comprising static dissipating fibers.

19. The article of claim 18 wherein the static dissipating fibers are metallic or carbon fibers.

20. The article of claim 10 wherein the article exhibits at least one of the following tests: a) response to flame propagation, upon direct exposure to flame, graded as A grade as per DIN EN 531:02.95 standard norm (DIN ISO15025:02.03 standard testing method); b) heat transmission on exposure to flame performances graded as B1 grade or higher (B2, B3, B4 or B5) as per DIN EN 531:02.95 standard norm (DIN EN 367:11.92 standard testing method); or c) heat transmission on exposure to radiant heat graded as C1 or higher (C2, C3, or C4), as per DIN EN 531:02.95 standard norm (DIN EN 366:05.93 standard testing method).

21. The article of claim 20 wherein the article meets all of the tests.

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