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(54) Title: LIMITED-ANTIMONY-CONTENT AND ANTIMONY-FREE MODACRYLIC / ARAMID BLENDS FOR IM-
PROVED FLASH FIRE AND ARC PROTECTION

(57) Abstract: A yarn, fabric, and garment suitable for use in arc and flame protection comprising aramid fiber and modacrylic fiber wherein the modacrylic fiber has less than 1.5 percent antimony and is preferably antimony-free. In one embodiment, the yarn, fabric, and/or garments consist essentially of (a) 50 to 80 weight percent meta-aramid fiber having a degree of crystallinity of at least 20%, (b) 10 to 40 weight percent modacrylic fiber that is antimony-free, (c) 5 to 20 weight percent para-aramid fiber, and (d) 1 to 3 weight percent antistatic fiber, based on the total weight of components (a), (b), (c) and (d). In some embodiments, garments made from the yarns provide thermal protection such that a wearer would experience less than a 65 percent predicted body burn when exposed to a flash fire exposure of 4 seconds per ASTM F1930, while maintaining a Category 2 arc rating per ASTM F1959 and NFPA 70E.



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TITLE OF INVENTION

5 LIMITED-ANTIMONY-CONTENT AND ANTIMONY-FREE MODACRYLIC /
ARAMID BLENDS FOR IMPROVED FLASH FIRE AND ARC PROTECTION

BACKGROUND OF THE INVENTION

10 **1. Field of the Invention**

This invention relates to a yarn useful for the production of protective fabrics and garments, and fabrics and garments that possess not only arc and flame protective properties, but also improved performance when exposed to flash fires.

15 **2. Description of Related Art**

When protecting workers from potential flash fires with protective apparel, the time of exposure to actual flame is an important consideration. Generally the term "flash" fire is used because the exposure to flame is of
20 very short duration, on the order of seconds. Further, while the difference in a single second seems small, when exposed to fire, an additional second of exposure to a flame can mean a tremendous difference in the burn injury.

The performance of a material in a flash fire can be measured using an instrumented mannequin using the test protocol of ASTM F1930. The
25 mannequin is clothed in the material to be measured, and then exposed to flames from burners; temperature sensors distributed throughout the mannequin measure the local temperature experienced by the mannequin that would be the temperatures experienced by a human body if subjected to the same amount of flames. Given a standard flame intensity, the extent of
30 the burns that would be experienced by a human, (i.e., first degree, second degree, etc.) and the percent of the body burned can be determined from the mannequin temperature data.

United States Patent No. 7,348,059 to Zhu et al. discloses modacrylic/aramid fiber blends for use in arc and flame protective fabrics and
35 garments. Such blends have on average a high content (40-70 weight percent) modacrylic fiber and lower content (10 to 40 weight percent) meta-aramid fiber having a degree of crystallinity of at least 20 %, and para-aramid

fiber (5 to 20 weight percent). Fabrics and garments made from such blends provide protection from electrical arcs and exposures to flash fires up to 3 seconds. United States Patent Application Publication US2005/0025963 to Zhu discloses an improved fire retardant blend, yarn, fabric and article of clothing made from a blend of 10-75 parts of at least one aramid staple fiber, 15 to 80 parts by weight of at least one modacrylic staple fiber, and 5 to 30 parts by weight of at least one aliphatic polyamide staple fiber. This blend will not provide a Category 2 arc rating for fabrics in the range of 186.5 to 237 grams per square meter (5.5 to 7 ounces per square yard) because of the high proportion of flammable aliphatic polyamide fiber in this blend. United States Patent 7,156,883 to Lovasic et al. discloses a fiber blend, fabrics, and protective garments comprising amorphous meta-aramid fiber, crystallized meta-aramid fiber, and flame retardant cellulosic fiber, the meta-aramid fiber being 50 to 85 weight percent with one to two thirds of the meta-aramid fiber being amorphous and with two to one third of the meta-aramid fiber being crystalline. Again, fabrics made by these blends would not provide a Category 2 arc rating for fabrics in the range of 186.5 to 237 grams per square meter (5.5 to 7 ounces per square yard).

The minimum performance required for flash fire protective apparel, per the NFPA 2112 standard, is less than 50% body burn from a 3 second flame exposure. Since flash fire is a very real threat to workers in some industries, and it is not possible to fully anticipate how long the individual will be engulfed in flames, any improvement in the flash fire performance of protective apparel fabrics and garments has the potential to save lives. In particular, if the protective apparel can provide enhanced protection to fire exposure above 3 seconds, e. g. 4 seconds or more, this represents an increase in potential exposure time of as much as 33% or more. Flash fires represent one of the most extreme types of thermal threat a worker can experience; such threats are much more severe than the simple exposure to a flame.

United States Patent application Ser. No. 12/218215 filed July 11, 2008, to Zhu relates to yarn for use in arc and flame protection, and fabrics and garments made from that yarn, the yarn consisting essentially of from (a) 50 to 80 weight percent meta-aramid fiber having a degree of crystallinity of at

least 20%, (b) 10 to 30 weight percent modacrylic fiber, (c) 5 to 20 weight percent para-aramid fiber, and (d) 1 to 3 weight percent antistatic fiber based on the total weight of components (a), (b), (c) and (d). The fabrics and garments have a basis weight in the range of 186.5 to 237 grams per square meter (5.5 to 7 ounces per square yard). In one embodiment, garments made from the yarn provide thermal protection such that a wearer would experience less than a 65 percent predicted body burn when exposed to a flash fire exposure of 4 seconds per ASTM F1930, while maintaining a Category 2 arc rating. The modacrylic fibers are said to include fibers having 2 to 40 weight percent antimony compounds; antimony is a known heavy metal with the potential for safe disposal considerations.

Arc and flame protection deals with the saving of human life, therefore any improvement that provides the combination of improved flash fire performance with a high level of arc protection at a low basis weight is desired. Especially desired is any improvement that also provides a potentially reduced environmental footprint.

SUMMARY OF THE INVENTION

This invention relates to yarn, fabrics, and garments for use in arc and flame protection comprising aramid fiber and modacrylic fiber wherein the modacrylic fiber has less than 1.5 percent antimony and in some embodiments is antimony-free. In one preferred embodiment, the yarn, fabric, and/or garment consist essentially of (a) 50 to 80 weight percent meta-aramid fiber having a degree of crystallinity of at least 20%, (b) 10 to 40 weight percent modacrylic fiber that is antimony-free, (c) 5 to 20 weight percent para-aramid fiber, and (d) 1 to 3 weight percent antistatic fiber, based on the total weight of components (a), (b), (c), and (d).

This invention also relates to a fabric suitable for use in arc and flame protection and garments made from that fabric, the fabric comprising aramid fiber and modacrylic fiber wherein the modacrylic fiber has less than 1.5 percent antimony and in some embodiments is antimony-free, the fabric having a basis weight in the range of 135 to 407 grams per square meter (4.0 to 12 ounces per square yard). In one embodiment, the aforementioned

garments provide thermal protection equivalent to less than a 65 % body burn at a 4 sec flame exposure per ASTM F1930, while maintaining a Category 2 arc rating per ASTM F1959 and NFPA 70E.

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DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, this invention relates to providing a yarn comprising a blend of aramid and modacrylic fibers from which fabrics and garments can be produced that provide surprisingly superior arc protection.

10 While antimony has traditionally been used as an additional fire retardant additive in modacrylic fiber, it is believed the yarn, fabric, and garments made from this blend of fibers has surprisingly superior arc performance even without increased amounts of antimony. In one embodiment, the modacrylic fibers have less than 1.5 percent antimony content, and in one preferred
15 embodiment the modacrylic fibers have less than 1.0 percent antimony content. In one most preferred embodiment, the modacrylic fibers are antimony-free, meaning that the fibers are made without the intentional addition of any antimony-based compounds that provide additional antimony content to the fiber over any trace amounts of antimony that might be in the
20 polymer. Use of these low-antimony content or antimony-free fibers provides fabrics that still provide protection while having the potential for less environmental disposal impact.

In one embodiment, fabrics and garments can be produced that provide surprisingly superior arc protection in excess of 1.5 calories per
25 square centimeter per ounce per square yard of fabric along with superior flash fire protection. Electrical arcs typically involve thousands of volts and thousands of amperes of electrical current, exposing the garment or fabric to intense incident energy. To offer protection to a wearer a garment or fabric must resist the transfer of this energy through to the wearer. It is believed that
30 this occurs by the fabric absorbing a portion of the incident energy and by the fabric resisting break-open, as well as the air-gap between fabric and wearer's body. During break-open a hole forms in the fabric directly exposing the surface or wearer to the incident energy.

In addition to resisting the intense incident energy from an electrical arc, the garments and fabrics also resist the thermal transfer of energy from a long exposure to a flash fire that is greater than 3 seconds. It is believed that this invention reduces energy transfer by absorbing a portion of the incident energy and by improved charring that allows a reduction in transmitted thermal energy.

In some embodiments, the yarn, fabric, or garment can consist essentially of a blend of meta-aramid fiber, modacrylic fiber, para-aramid fiber, and optionally antistatic fiber. Typically in one embodiment, yarns consist of 50 to 80 weight percent meta-aramid fiber with a degree of crystallinity of at least 20%, 10 to 40 weight percent modacrylic fiber, and 5 to 20 weight percent para-aramid fiber. If desired, optionally the blend can contain 1 to 3 weight percent antistatic fiber, which in some embodiments can replace the meta-aramid fiber, with the proviso that at least 50 weight percent meta-aramid fiber is maintained in this embodiment of the blend. Therefore in some preferred embodiments, yarns can consist, in weight percents, of a minimum of 50 percent and a maximum of 80 percent meta-aramid fiber, 10 to 40 percent modacrylic fiber that is antimony-free, 5 to 20 percent para-aramid fiber, and 1 to 3 percent antistatic fiber. Preferably, yarns consist essentially of at least 55 percent and a maximum of 70 percent meta-aramid fiber, 20 to 35 percent modacrylic fiber that is antimony-free, 5 to 15 percent para-aramid fiber, and 1 to 3 percent antistatic fiber. All of the above percentages are on a basis of the three named components, if three are present; or the four named components, if four are present. By "yarn" is meant an assemblage of fibers spun or twisted together to form a continuous strand that can be used in weaving, knitting, braiding, or plaiting, or otherwise made into a textile material or fabric. In some embodiments, the blend consists essentially of the previously recited amounts. As used herein "consisting essentially of" encompasses the use of various chemical additives in the polymer used in the fibers in amounts up to about 25%.

As used herein, "aramid" is meant a polyamide wherein at least 85% of the amide (-CONH-) linkages are attached directly to two aromatic rings. Additives can be used with the aramid and, in fact, it has been found that up to as much as 10 percent, by weight, of other polymeric material can be

blended with the aramid or that copolymers can be used having as much as 10 percent of other diamine substituted for the diamine of the aramid or as much as 10 percent of other diacid chloride substituted for the diacid chloride of the aramid. Suitable aramid fibers are described in Man-Made Fibers--

- 5 Science and Technology, Volume 2, Section titled Fiber-Forming Aromatic Polyamides, page 297, W. Black et al., Interscience Publishers, 1968. Aramid fibers are, also, disclosed in U.S. Pat. Nos. 4,172,938; 3,869,429; 3,819,587; 3,673,143; 3,354,127; and 3,094,511. Meta-aramids are those aramids where the amide linkages are in the meta-position relative to each other, and
10 para-aramids are those aramids where the amide linkages are in the para-position relative to each other. The aramids most often used are poly(metaphenylene isophthalamide) and poly(paraphenylene terephthalamide).

- When used in yarns, the meta-aramid fiber provides a flame resistant
15 char forming fiber with an Limiting Oxygen Index (LOI) of about 26. Meta-aramid fiber is also resistant to the spread of damage to the yarn due to exposure to flame. Because of its balance of modulus and elongation physical properties, meta-aramid fiber also provides for a comfortable fabric useful in single-layer fabric garments meant to be worn as industrial apparel in
20 the form of conventional shirts, pants, and coveralls. It is critical that the yarn has at least 50 weight percent meta-aramid fiber to provide improved char to lightweight fabrics and garments to resist the thermal transfer of energy during extended exposure to flash fires. In some preferred embodiments, the yarn has at least 55 weight percent meta-aramid fibers. In some embodiments, the
25 preferred maximum amount of meta-aramid fibers is 70 weight percent or less; however, amounts as high as 80 weight percent can be used.

- By modacrylic fiber it is meant acrylic synthetic fiber made from a polymer comprising primarily acrylonitrile. Preferably the polymer is a copolymer comprising 30 to 70 weight percent of a acrylonitrile and 70 to 30
30 weight percent of a halogen-containing vinyl monomer. The halogen-containing vinyl monomer is at least one monomer selected, for example, from vinyl chloride, vinylidene chloride, vinyl bromide, vinylidene bromide, etc. Examples of copolymerizable vinyl monomers are acrylic acid, methacrylic

acid, salts or esters of such acids, acrylamide, methacrylamide, vinyl acetate, etc.

The preferred modacrylic fibers are made from copolymers of acrylonitrile combined with vinylidene chloride, the copolymer having in addition either less than 1.5 weight percent antimony oxide or antimony oxides, or the copolymer being totally free of antimony. Such useful modacrylic fibers can be made by processes that include, but are not limited to, fiber manufacturing processes similar to those that disclose the addition of antimony compounds of a higher percentage during manufacture. In such cases, very low antimony content fibers and antimony-free fibers can be made by restricting the amount of, or eliminating entirely, any antimony compounds added to the copolymer during manufacture. Representative processes that can be modified in this manner are disclosed in United States Patent No. 3,193,602 having 2 weight percent antimony trioxide, fibers disclosed in United States Patent No. 3, 748,302 made with various antimony oxides that are present in an amount of at least 2 weight percent and preferably not greater than 8 weight percent, and fibers disclosed in United States Patent Nos. 5,208,105 & 5,506,042 having 8 to 40 weight percent of an antimony compound.

In some embodiments, within the yarns modacrylic fiber provides a flame resistant char forming fiber with an LOI typically at least 26. In one preferred embodiment the modacrylic fiber has a LOI of at least 26 while also being antimony-free. Modacrylic fiber is also resistant to the spread of damage to the yarn due to exposure to flame. Modacrylic fiber while highly flame resistant does not by itself provide adequate tensile strength to a yarn, or fabric made from the yarn, to offer the desired level of break-open resistance when exposed to an electrical arc. The yarn has at least 10 weight percent modacrylic fiber and in some preferred embodiments the yarn has at least 15 weight percent modacrylic fiber. In some embodiments, the preferred maximum amount of modacrylic fiber is 40 weight percent or less.

In some embodiments, the meta-aramid fiber has a certain minimum degree of crystallinity to realize the improvement in arc protection. The degree of crystallinity of the meta-aramid fiber is at least 20% and more preferably at least 25%. For purposes of illustration due to ease of formation of the final

fiber a practical upper limit of crystallinity is 50% (although higher percentages are considered suitable). Generally, the crystallinity will be in a range from 25 to 40%. An example of a commercial meta-aramid fiber having this degree of crystallinity is Nomex® T-450 or T-300 available from E. I. du Pont de

5 Nemours & Company of Wilmington, Delaware.

The degree of crystallinity of an meta-aramid fiber is determined by one of two methods. The first method is employed with a non-voided fiber while the second is on a fiber that is not totally free of voids.

The percent crystallinity of meta-aramids in the first method is
 10 determined by first generating a linear calibration curve for crystallinity using good, essentially non-voided samples. For such non-voided samples the specific volume (1/density) can be directly related to crystallinity using a two-phase model. The density of the sample is measured in a density gradient column. A meta-aramid film, determined to be non-crystalline by x-ray
 15 scattering methods, was measured and found to have an average density of 1.3356 g/cm³. The density of a completely crystalline meta-aramid sample was then determined from the dimensions of the x-ray unit cell to be 1.4699 g/cm³. Once these 0% and 100% crystallinity end points are established, the crystallinity of any non-voided experimental sample for which the density is
 20 known can be determined from this linear relationship:

$$\text{Crystallinity} = \frac{(1/\text{non-crystalline density}) - (1/\text{experimental density})}{(1/\text{non-crystalline density}) - (1/\text{fully-crystalline density})}$$

25 Since many fiber samples are not totally free of voids, Raman spectroscopy is the preferred method to determine crystallinity. Since the Raman measurement is not sensitive to void content, the relative intensity of the carbonyl stretch at 1650-1 cm can be used to determine the crystallinity of a meta-aramid in any form, whether voided or not. To accomplish this, a
 30 linear relationship between crystallinity and the intensity of the carbonyl stretch at 1650 cm⁻¹, normalized to the intensity of the ring stretching mode at 1002 cm⁻¹, was developed using minimally voided samples whose crystallinity was previously determined and known from density measurements as described above. The following empirical relationship,

which is dependent on the density calibration curve, was developed for percent crystallinity using a Nicolet Model 910 FT-Raman Spectrometer:

5 % crystallinity = 100.0 x $\frac{(I(1650 \text{ cm}^{-1}) - 0.2601)}{0.1247}$

where $I(1650 \text{ cm}^{-1})$ is the Raman intensity of the meta-aramid sample at that point. Using this intensity the percent crystallinity of the experiment sample is calculated from the equation.

10 Meta-aramid fibers, when spun from solution, quenched, and dried using temperatures below the glass transition temperature, without additional heat or chemical treatment, develop only minor levels of crystallinity. Such fibers have a percent crystallinity of less than 15 percent when the crystallinity of the fiber is measured using Raman scattering techniques. These fibers
15 with a low degree of crystallinity are considered amorphous meta-aramid fibers that can be crystallized through the use of heat or chemical means. The level of crystallinity can be increased by heat treatment at or above the glass transition temperature of the polymer. Such heat is typically applied by contacting the fiber with heated rolls under tension for a time sufficient to
20 impart the desired amount of crystallinity to the fiber.

 The level of crystallinity of m-aramid fibers can be increased by a chemical treatment, and in some embodiments this includes methods that color, dye, or mock dye the fibers prior to being incorporated into a fabric. Some methods are disclosed in, for example, United States Patents
25 4,668,234; 4,755,335; 4,883,496; and 5,096,459. A dye assist agent, also known as a dye carrier may be used to help increase dye pick up of the aramid fibers. Useful dye carriers include aryl ether, benzyl alcohol, or acetophenone.

 Para-aramid fibers provide a high tensile strength fiber, that when
30 added in adequate amounts in the yarn, improves the break-open resistance of fabrics formed from the yarn after flame exposure. In some embodiments, the yarn has at least 5 weight percent para-aramid fibers. Large amounts of para-aramid fibers in the yarns can make garments comprising the yarns uncomfortable to the wearer. In some embodiments, the preferred maximum

amount of para-aramid fibers is 15 weight percent or less; however, amounts as high as 20 weight percent can be used.

The term tensile strength refers to the maximum amount of stress that can be applied to a material before rupture or failure. The tear strength is the amount of force required to tear a fabric. In general the tensile strength of a fabric relates to how easily the fabric will tear or rip. The tensile strength can also relate to the ability of the fabric to avoid becoming permanently stretched or deformed. The tensile and tear strengths of a fabric should be high enough so as to prevent ripping, tearing, or permanent deformation of the garment in a manner that would significantly compromise the intended level of protection of the garment.

Because static electrical discharges can be hazardous for workers working with sensitive electrical equipment or near flammable vapors, the yarn, fabric, or garment optionally contains an antistatic component comprising a metal or carbon. Illustrative examples are steel fiber, carbon fiber, or a carbon combined with an existing fiber. When used, the antistatic component is present in an amount of 1 to 3 weight percent of the total yarn, fabric, or garment; and if desired can replace an equivalent weight of meta-aramid fiber in the yarn, fabric, or garment. In some preferred embodiments the antistatic component is present in an amount of only 2 to 3 weight percent. U.S. Patent 4,612,150 (to De Howitt) and U.S. Patent 3,803,453 (to Hull) describe an especially useful conductive fiber wherein carbon black is dispersed within a thermoplastic fiber, providing anti-static conductance to the fiber. The preferred antistatic fiber is a carbon-core nylon-sheath fiber. Use of anti-static fibers provides yarns, fabrics, and garments having reduced static propensity, and therefore, reduced apparent electrical field strength and nuisance static.

Yarns can be produced by yarn spinning techniques such as but not limited to ring spinning, core spinning, and air jet spinning, including air spinning techniques such as Murata air jet spinning where air is used to twist staple fibers into a yarn. If single yarns are produced, they are then preferably plied together to form a ply-twisted yarn comprising at least two single yarns prior to being converted into a fabric.

To provide protection from the intense thermal stresses caused by electrical arcs it is desirable that an arc protective fabric and garments formed from that fabric possess features such as an LOI above the concentration of oxygen in air (that is, greater than 21 and preferably greater than 25) for flame resistance, a short char length indicative of slow propagation of damage to the fabric, and good break-open resistance to prevent incident energy from directly impinging on the surfaces below the protective layer.

The term fabric, as used in the specification and appended claims, refers to a desired protective layer that has been woven, knitted, or otherwise assembled using one or more different types of the yarn previously described. A preferred embodiment is a woven fabric, and a preferred weave is a twill weave. In some preferred embodiments the fabrics have an arc resistance, normalized for basis weight, of greater than 1.5 calories per square centimeter per ounce per square yard (0.185 joules per square centimeter per grams per square meter). In some embodiments the arc resistance normalized for basis weight is preferably at least 1.7 calories per square centimeter per ounce per square yard (0.21 joules per square centimeter per grams per square meter).

In some fabric embodiments, yarns having the proportions of meta-aramid fiber, modacrylic fiber, para-aramid fiber, and optionally antistatic fiber as previously described, are preferably exclusively present in the fabric.. In the case of a woven fabric the yarns are used in both the warp and fill of the fabric. If desired, the relative amounts of meta-aramid fiber, modacrylic fiber, para-aramid fiber and antistatic fiber can vary in the yarns as long as the composition of the yarns falls within the previously described ranges.

In some embodiments, the fabric can have, in addition, up to as much as 20 percent by weight nylon fiber for improved durability of the fabric. In some preferred embodiments the nylon is present in an amount of 10 percent or less, with some preferred embodiments being 5 percent or less. The nylon fiber can be incorporated as a separate yarn in the fabric, such as a ripstop yarn, or as an additional staple fiber in the staple fiber blend.

In some fabric embodiments that include nylon fiber, the overall proportions of modacrylic fiber in the fabric can be increased to ensure adequate arc resistance is achieved. Such fabrics, can have 50 to 70 weight percent modacrylic fiber, 25 to 40 percent aramid fiber, and 1 to 20 percent

nylon fiber, based on the overall amounts of those three general types of fibers that are present, with the aramid fiber being para-aramid and meta-aramid present in a ratio of roughly 1:2 to 1:3. In the most preferred embodiments, the modacrylic fiber is antimony-free.

5 In some embodiments, garments made from the fibers previously described, especially those with antimony-free modacrylic fiber, provide thermal protection to the wearer that is equivalent to less than a 65 percent predicted body burn when exposed to a flash fire of 4 seconds while maintaining a Category 2 arc rating. This is a significant improvement over the
10 minimum standard of less than a 50 percent predicted body burn to the wearer at a 3 second exposure; burn injury is essentially exponential in nature with respect to flame exposure for some other flame resistance fabrics. The protection provided by the garment, should there be an additional second of flame exposure time, can potentially mean the difference between life and
15 death.

 There are two common category rating systems for arc ratings. The National Fire Protection Association (NFPA) has 4 different categories with Category 1 having the lowest performance and Category 4 having the highest performance. Under the NFPA 70E system, Categories 1,2,3, and 4
20 correspond to a heat flux through the fabric of 4, 8, 25, and 40 calories per square centimeter, respectively. The National Electric Safety Code (NESC) also has a rating system with 3 different categories with Category 1 having the lowest performance and Category 3 having the highest performance. Under the NESC system, Categories 1,2, and 3 correspond to a heat flux through
25 the fabric of 4, 8, and 12 calories per square centimeter, respectively. Therefore, a fabric or garment having a Category 2 arc rating can withstand a thermal flux of 8 calories per square centimeter, as measured per standard set method ASTM F1959.

 The performance of the garments in a flash fire is measured using an
30 instrumented mannequin using the test protocol of ASTM F1930. The mannequin is clothed in the garment and exposed to flames from burners and sensors measure the localized skin temperatures that would be experienced by a human body if subjected to the same amount of flames. Given a standard flame intensity, the extent of the burns that would be

experienced by a human, (i.e., first degree, second degree, etc.) and the percent of the body burned can be determined from the mannequin temperature data. A low predicted body burn is an indication of better protection of the garment in flash fire hazard.

5 It is believed the use of crystalline meta-aramid fiber in the yarns, fabrics, and garments as previously described not only can provide improved performance in flash fires, but also results in significantly reduced laundry shrinkage. This reduced shrinkage is based on an identical fabric wherein the only difference is the use of meta-aramid fiber having the degree of
10 crystallinity set forth previously compared to an meta-aramid fiber that has not been treated to increase crystallinity. For purposes herein shrinkage is measured after a wash cycle of 20 minutes with a water temperature of 140°F. Preferred fabrics demonstrate a shrinkage of 5 percent or less after 10 wash cycles and preferably after 20 cycles. As the amount of fabric per unit area
15 increases, the amount of material between a potential hazard and the subject to be protected increases. An increase in fabric basis weight results in increased break-open resistance, increased thermal protection factor, and increased arc protection; however it is not evident how improved performance can be achieved with lighter weight fabrics. The combinations of meta-aramid
20 fiber, modacrylic fiber (preferably antimony-free modacrylic fiber), para-aramid fiber, and antistatic fiber used in yarns as previously described allow the use of lighter weight fabrics in protective apparel, particularly in more comfortable single fabric garments, with improved performance. In some embodiments, the basis weight of fabrics that have both the desired arc and flash fire
25 performance is 135 g/m² (4 oz/yd²) or greater, and in some embodiments the basis weight is 186.5 g/m² (5.5 oz/yd²) or greater. In some preferred embodiments the basis weight is 200 g/m² (6.0 oz/yd²) or greater. In some embodiments, the preferred maximum basis weight is 237 g/m² (7.0 oz/yd²); in some other embodiments, the maximum basis weight is 407 g/m² (12
30 oz/yd²) Above this maximum the comfort benefits of the lighter weight fabric in single fabric garments is believed to be reduced, because it is believed higher basis weight fabric would show increased stiffness.

Char length is a measure of the flame resistance of a textile. A char is defined as a carbonaceous residue formed as the result of pyrolysis or

incomplete combustion. The char length of a fabric under the conditions of test of ASTM 6413-99 as reported in this specification is defined as the distance from the fabric edge that is directly exposed to the flame to the furthest point of visible fabric damage after a specified tearing force has been applied. Per NFPA 2112, a flash fire standard, the fabric should have a char length of less than 4 inches (10.2 cm). Per ASTM F1506, an arc resistance standard, the fabric should have a char length of less than 6 inches.

Therefore, in one embodiment, the fabric has a char length as measured by ASTM 6413-99 of less than 6 inches (15.2 cm). In another embodiment, the fabric has a char length as measured by ASTM 6413-99 of less than 4 inches (10.2 cm)

In some preferred embodiments, the fabric is used as a single layer in a protective garment. Within this specification the protective value of a fabric is reported for a single layer of that fabric. In some embodiments this invention also includes a multi-layer garment made from the fabric.

In some particularly useful embodiments, fabric suitable for use in arc and flame protection comprises aramid fiber and modacrylic fiber wherein the modacrylic fiber has less than 1.5 percent antimony and in some embodiments has less than 1 percent antimony and in some embodiments is antimony-free. Spun staple yarns containing the fibers previously described can be used to make flame-resistant fabrics and garments, and in some embodiments these fabrics and garment contain antistatic fibers as previously described. In some embodiments the preferred basis weight of fabrics in these garments is 150 g/m^2 (4.5 oz/yd^2) or greater. In some embodiments, the preferred maximum basis weight is 290 g/m^2 (8.5 oz/yd^2).

In some embodiments the garments can have essentially one layer of the protective fabric made from the spun staple yarn. Exemplary garments of this type include jumpsuits and coveralls for fire fighters or for military personnel. Such suits are typically used over the firefighters clothing and can be used to parachute into an area to fight a forest fire. Other garments can include pants, shirts, gloves, sleeves and the like that can be worn in situations such as chemical processing industries or industrial electrical/utility where an extreme thermal event might occur.

TEST METHODS

The abrasion performance of fabrics is determined in accordance with ASTM D-3884-01 "Standard Guide for Abrasion Resistance of Textile Fabrics (Rotary Platform, Double Head Method)".

The arc resistance of fabrics is determined in accordance with ASTM F-1959-99 "Standard Test Method for Determining the Arc Thermal Performance Value of Materials for Clothing".

The antimony content in the modacrylic fiber is determined on a sample of the fabric, since none of the other fibers are provided with antimony as disclosed in their Material Safety Data Sheet. A 0.1 gram sample is obtained from the fabric. The sample is combined first with four milliliters of environmental grade sulfuric acid and then an additional two milliliters of environmental grade nitric acid is added. The sample in acid is heated in a microwave for approximate 2 minutes at a temperature 200-220C to digest the nonmetallic materials. The acid digestate solution is diluted to 100 milliliters in a Class A volumetric flask with Milli-Q Water. The acid solution is then analyzed by ICP Emission Spectrometry using three emission wavelengths at 206.836nm, 217.582nm, and 231.146nm to determine the antimony content.

The break strength of fabrics is determined in accordance with ASTM D-5034-95 "Standard Test Method for Breaking Strength and Elongation of Fabrics (Grab Test)".

The limited oxygen index (LOI) of fabrics is determined in accordance with ASTM G-125-00 "Standard Test Method for Measuring Liquid and Solid Material Fire Limits in Gaseous Oxidants".

The tear resistance of fabrics is determined in accordance with ASTM D-5587-03 "Standard Test Method for Tearing of Fabrics by Trapezoid Procedure".

The thermal protection performance of fabrics is determined in accordance with NFPA 2112 "Standard on Flame Resistant Garments for Protection of Industrial Personnel Against Flash Fire". The term thermal protective performance (or TPP) relates to a fabric's ability to provide

continuous and reliable protection to a wearer's skin beneath a fabric when the fabric is exposed to a direct flame or radiant heat.

Flash fire protection level testing was done according to ASTM F-1930 using an instrumented thermal mannequin with standard pattern coverall

5 made with the test fabric.

The char length of fabrics is determined in accordance with ASTM D-6413-99 "Standard Test Method for Flame Resistance of Textiles (Vertical Method)".

10 The minimum concentration of oxygen, expressed as a volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a fabrics initially at room temperature is determined under the conditions of ASTM G125 / D2863.

Shrinkage is determined by physically measuring unit area of a fabric after one or more wash cycles. A cycle denotes washing the fabric in an
15 industrial washing machine for 20 minutes with a water temperature of 140 degrees F.

To illustrate the present invention, the following examples are provided. All parts and percentages are by weight and degrees in Celsius unless
20 otherwise indicated.

Example 1

This example illustrates the surprising increase in fabric arc rating with the use of antimony-free modacrylic fiber. A durable arc and thermal
25 protective fabric (Item 1) is prepared having in the both warp and fill airjet spun yarns of intimate blends of Nomex® type 300 fiber, Kevlar® 29 fiber, and antimony-free modacrylic fiber. Nomex® type 300 is poly(m-phenylene isophthalamide)(MPD-I) having a degree of crystallinity of 33-37%. The modacrylic fiber is ACN/polyvinylidene chloride co-polymer fiber having no
30 measured antimony (known commercially as Modacrylic SE made by Keneka). The Kevlar® 29 fiber is poly(p-phenylene terephthalamide) (PPD-T) fiber.

A picker blend sliver of 65 weight percent of Nomex® type 300 fiber, 10 weight percent of Kevlar® 29 fiber, and 25 weight percent of modacrylic fiber

is prepared and is made into spun staple yarn using cotton system processing and an airjet spinning frame. The resultant yarn is a 21 tex (28 cotton count) single yarn. Two single yarns are then plied on a plying machine to make a two-ply yarn having 10 turns/inch twist.

- 5 The yarn is then used as in the warp and fill of a fabric that is made on a shuttle loom in a 3x1 twill construction. The greige twill fabric has a basis weight of 224 g/m² (6.6 oz/yd²). The greige twill fabric is then scoured in hot water and is jet dyed using basic dye and dried. The finished twill fabric has a construction of 31 ends x 16 picks per cm (77 ends x 47 picks per inch) and a
10 basis weight of 224 g/m² (6.6 oz/yd²).

A comparison yarn and fabric (Item A) are then made with the only difference being the modacrylic fiber has a nominal 7% antimony (known commercially as Protex®C).

- One portion of each of the two fabrics is then tested for arc, thermal
15 and mechanical properties, and another portion of each of the two fabrics is converted into single-layer protective coveralls for flash fire testing. Arc testing performance is shown in Table 1. Both fabrics have both the desired arc rating of Category 2 per ASTM F1959 and NFPA 70E and a instrumented thermal mannequin predicted body burn at 4 seconds per ASTM F1930
20 exposure of less than 65%. However, surprisingly, the fabric containing the antimony-free modacrylic has an arc resistance that was 14% greater than the fabric having 7% antimony modacrylic.

Table 1

Item	Meta-Aramid (wt. %)	Para-Aramid (wt. %)	Modacrylic (wt. %)	Antimony Content (%)	Basis Weight (oz/yd ²)	Arc Rating (cal/cm ²)	Arc Resistance (cal/cm ² /oz/yd ²)
1	65	10	25	0	6.6	10.3	1.6
A	65	10	25	7	6.6	9.1	1.4

25

Example 2

The general procedure of Example 1 is repeated to make and test three different fabrics and garments, except that three different modacrylic

- fibers were used and nylon fiber was also included in the yarn blend. Item 2 contains modacrylic fiber having a low antimony content of 1.2% (made by Fushun Rayva Fiber Company, Wanghua District, Fushun, China). Item B contains modacrylic fiber having an antimony content of 9.9% (known commercially as Protex®C). Item C contains modacrylic fiber having an antimony content of 4.1% (known commercially as Protex®M). The fiber compositions and arc testing performance is shown in Table 2.

Table

	Meta-Aramid (wt. %)	Para-Aramid (wt. %)	Nylon (wt. %)	Modacrylic (wt. %)	Antimony Content (%)	Basis Weight (oz/yd²)	Arc Rating (cal/cm²)	Arc Resistance (cal/cm²/oz)
	20	10	10	60	1.2	9.6	17.6	1.8
	25	10	5	60	4.1	8.7	11.4	1.3
	25	10	5	60	9.9	8.7	9.8	1.1

Example 3

- Examples 1 and 2 are repeated except 2 weight percent of the Nomex® meta-aramid fiber is replaced with an antistatic fiber that is a carbon-core nylon-sheath fiber known commercially as P140. The resultant fabric is converted into single-layer protective coveralls with predicted performance similar to Examples 1 & 2.

CLAIMS**What is claimed is:**

- 5 1. A yarn for use in arc and flame protection comprising aramid fiber and modacrylic fiber wherein the modacrylic fiber has less than 1.5 percent antimony.
2. The yarn of claim 1 wherein the modacrylic fiber has less than 1
10 percent antimony.
3. The yarn of claim 2 wherein the modacrylic fiber is antimony-free.
- 15 4. The yarn of claim 3 further comprising an antistatic fiber.
5. The yarn of claim 3 consisting essentially of:
 (a) 50 to 80 weight percent meta-aramid fiber having a
 degree of crystallinity of at least 20%;
20 (b) 10 to 40 weight percent modacrylic fiber;
 (c) 5 to 20 weight percent para-aramid fiber; and
 (d) 1 to 3 weight percent antistatic fiber;
said percentages on the basis of components (a), (b), (c), and (d).
- 25 6. A fabric suitable for use in arc and flame protection comprising aramid fiber and modacrylic fiber wherein the modacrylic fiber has less than 1.5 percent antimony; the fabric having a basis weight of 135 to 407 grams per square meter (4.0 to 12 ounces per square yard).
- 30 7. The fabric of claim 6 wherein the modacrylic fiber has less than 1 percent antimony.
8. The fabric of claim 6 wherein the modacrylic fiber is antimony-free.

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9. The fabric of claim 8 further comprising an antistatic fiber.

10. The fabric of claim 8 comprising a yarn consisting essentially of:

- 5 (a) 50 to 80 weight percent meta-aramid fiber having a degree of crystallinity of at least 20%;
- (b) 10 to 40 weight percent modacrylic fiber;
- (c) 5 to 20 weight percent para-aramid fiber; and
- (d) 1 to 3 weight percent antistatic fiber;

10 said percentages on the basis of components (a), (b), (c), and (d); the fabric having a basis weight of 150 to 290 grams per square meter (4.5 to 8.5 ounces per square yard).

11. The fabric of claim 8 having arc resistance according to ASTM F-1959-99 of at least 1.5 calories per square centimeter per ounce per square
15 yard of fabric.

12. The fabric of claim 8 further comprising a nylon fiber.

13. The fabric of claim 12 having arc resistance according to ASTM F-1959-99 of at least 1.7 calories per square centimeter per ounce per square
20 yard of fabric.

14. A garment comprising the fabric of claim 11 providing thermal protection equivalent to less than a 65 % body burn at a 4 sec flame exposure
25 per ASTM F1930, while maintaining a Category 2 arc rating per ASTM F1959 and NFPA 70E.

15. A garment comprising the fabric of claim 13 providing thermal protection equivalent to less than a 65 % body burn at a 4 sec flame exposure
30 per ASTM F1930, while maintaining a Category 2 arc rating per ASTM F1959 and NFPA 70E.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/037028

A. CLASSIFICATION OF SUBJECT MATTER

INV. D02G3/44

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D02G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/026481 A1 (DU PONT [US]; ZHU REIYAO [US]; GUCKERT DEBBIE [US]; GABARA VLODEK [US]) 26 February 2009 (2009-02-26) page 6, line 33 - page 7, line 22; claim 8 page 9, line 27 - page 10, line 17 page 11, line 11 - line 13 -----	1-15
X	WO 2005/090660 A1 (DU PONT [US]; ZHU REIYAO [US]) 29 September 2005 (2005-09-29) page 3, line 4 - page 5, line 2; claims 1-3 page 7, line 13 - line 15 page 6, line 20 - line 22 ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/116043 A1 (HOPE DOUG [US] ET AL) 1 June 2006 (2006-06-01) paragraph [0025] paragraph [0030]; table 2 -----	1-15
X	EP 0 940 487 A2 (BASF CORP [US]) 8 September 1999 (1999-09-08) paragraph [0020] - paragraph [0025]; claims 1-5 -----	1-15
A	EP 0 076 971 A1 (BAYER AG [DE]) 20 April 1983 (1983-04-20) page 8, line 6 - line 24; claim 4; table 1 -----	1-3,6-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/037028

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009026481 A1	26-02-2009	CA 2694361 A1 CN 101784704 A EP 2181209 A1 KR 20100059883 A US 2009053957 A1	26-02-2009 21-07-2010 05-05-2010 04-06-2010 26-02-2009
WO 2005090660 A1	29-09-2005	BR PI0508166 A CA 2557185 A1 CN 1930334 A EP 1725704 A1 JP 2007529649 T KR 20060124761 A US 2005208855 A1	07-08-2007 29-09-2005 14-03-2007 29-11-2006 25-10-2007 05-12-2006 22-09-2005
US 2006116043 A1	01-06-2006	CN 101263253 A	10-09-2008
EP 0940487 A2	08-09-1999	CA 2262850 A1 CN 1477243 A CN 1241446 A	06-09-1999 25-02-2004 19-01-2000
EP 0076971 A1	20-04-1983	DE 3140274 A1 JP 58074730 A US 4451423 A	28-04-1983 06-05-1983 29-05-1984